

**Feasibility Analysis of Solar Evaporation and Recovery of Dissolved Salts  
from Agricultural Drainage Water in the San Joaquin Valley**

- 1. Evaluation of Red Rock Ranch Pilot Test Program**
- 2. Proposed Control of Brine Chemistry during Evaporation**
- 3. Possible Uses of Intermediate Brine and Sodium Sulfate Product**
- 4. Onsite Storage of Mixed Agricultural Salts**

December 2004

Final report prepared under California Department of Water Resources Agreement  
No. 4600000534-01

by:

James L. Fairchild, P.E. Chemical #2957  
84830 12<sup>th</sup> St.  
Trona, California 93562-2520

## **Abstract**

The data from the pilot test at Red Rock Ranch clearly demonstrates that accumulated salt can be leached from soil and that future buildup of salt in the soil can be prevented. Furthermore, there is a vast acreage in the San Joaquin Valley that would benefit from active control of salt buildup in the soil. However, success in leaching salt from the soil creates the problem of disposing of the salt-laden water produced by leaching.

A method to analyze solar pond operations based on concentration ratios is introduced, using data from the Red Rock Ranch pilot test. The concentration ratios show that calcium and bicarbonate begin precipitating at the onset of evaporation and continue throughout the process. The ratios also show that all but sulfate continue to concentrate in the water at least as far as the evaporation-concentration has been tested.

The water leached from Red Rock Ranch soils is high in scale-forming salts. As the water is concentrated by solar evaporation, approximately 18% of the total dissolved solids will precipitate as scale on evaporation equipment. While it is technically possible to completely prevent scale formation, this will likely be prohibitively expensive, because it will cost nearly \$100 per acre-foot of water just for water treatment reagents. Even if scale were accepted during most of the evaporation step, treatment to prevent scale would be needed if the remaining salts are to be separated into salable quality product.

A sequence of process steps to separate sodium chloride, sodium sulfate, boric acid, magnesium oxide and potassium nitrate as salable products is proposed. While the separation technology appears to be feasible, the brine is unlike that anywhere else in the world, so the separation technology has never been demonstrated. Although the technology appears feasible, it has considerable uncertainty because even the fundamental solubility data have never been developed. There is also very high economic uncertainty in a project to commercially separate the agricultural waste salts.

A large scale (1 million tons per year) plant to process agricultural drainage salts will require an estimated ten years to research, develop, test, design and construct. While this is being done, it will be necessary to store the drainage salts in deep piles. With appropriate design, these storage piles can also be used to do the final evaporation of concentrated drainage water to crystallize the mixed waste salts.

The drift of mist out of the spray evaporation area appears to be a serious problem. This not only contaminates the soil around the spray pond, it also contributes particulates to the air in potential violation of air quality regulations. To date it does not appear that the potential regulatory issues related to air quality have been addressed, although these issues appear serious. A method based on multiple slatted fences is proposed as one way to control the drift of mist outside the spray area.

## **Table of Contents**

	Page
1.0 Evaluation of Red Rock Ranch Pilot Test Program	4
1.1 Analysis of Energy Supply	4
1.2 Air Quality - Particulate Emissions from Spray Evaporation Ponds	6
1.3 Brine Chemistry Description	9
1.3.1 Concentration Ratios	9
1.3.2 Molarities, Molar Concentration Products and Weight Percents	10
1.3.3 Brine Chemistry during Uncontrolled Brine Concentration	10
1.3.3.1 Precipitation of Calcium and Bicarbonate	10
1.3.3.2 Precipitation of Calcium Sulfate	12
1.3.3.3 Precipitation of Sodium Sulfate	13
1.3.3.4 Disposition of Selenium	13
1.3.3.5 Non-precipitating Constituents	13
1.4 Control Analyses during Solar Evaporation	14
1.4.1 Conductivity vs. Water Composition	14
1.4.2 Specific Gravity vs. Water Composition	14
1.5 Analyses of Minor Constituents	14
1.5.1 Strontium and Barium	14
1.5.2 Aluminum and Silica	15
1.5.3 Copper, Manganese, Molybdenum and Vanadium	15
1.5.4 Dissolved Organic Carbon	16
2.0 Proposed Control of Brine Chemistry during Evaporation	16
2.1 Control of Scaling in the Evaporator	16
2.2 Calcium Removal at Minimum Reagent Cost	18
2.3 Control of Sodium Sulfate Crystallization – Summer	18
2.4 Control of Sodium Sulfate Crystallization – Winter	19
2.5 Separation of Boric Acid	20
2.6 Separation of Magnesium Oxide	20
2.7 Separation of Sodium Chloride and Potassium Nitrate	20
2.8 Residual Brine	21
3.0 Possible Uses of Intermediate Brine and Sodium Sulfate Product	21
3.1 Solar Gradient Pond for Electric Power Generation	21
3.2 Traditional Sodium Sulfate Market	22
3.3 Other Possible Uses for Sodium Sulfate	22
3.3.1 Electrolysis to Produce NaOH and H <sub>2</sub> SO <sub>4</sub>	22
3.3.2 React with NH <sub>3</sub> and CO <sub>2</sub> to Make (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> and Na <sub>2</sub> CO <sub>3</sub>	24
3.3.3 React with KCl to Make K <sub>2</sub> SO <sub>4</sub>	25
4.0 Onsite Storage of Mixed Agricultural Salts	26
Appendix A Tables and Figures Concerning Red Rock Ranch Pilot Tests	
Appendix B References	

## **1.0 Evaluation of Red Rock Ranch Pilot Test Program**

### **1.1 Analysis of Energy Supply**

The evaporation of water requires heat. At a temperature of 85°F, a net of 1,045.55 BTU must be provided to evaporate one pound of water. This means that the quantity of water that will evaporate in any evaporation system will be directly proportional to the net heat absorbed from all sources (total absorbed less heat losses).

In the spray pond pilot test at Red Rock Ranch only two potentially significant sources of heat are available: solar radiation and the sensible heat extractable from moving air. Similarly, there are only two potentially significant mechanisms of heat loss: radiation to space at night and convective heat loss by warming cold air moving across the spray area. If the air is cooled by contact with warm brine, then the air is a heat source. But if the air is heated by contact with warm brine, then the air is a heat loss. Since it would be the same air in both cases, these two air terms can be combined into a single term that looks at the net temperature change of the air. Combining these heat sources as an equation gives:

$$Q_{\text{net}} = Q_{\text{solar}} + Q_{\text{air}} - Q_{\text{rad}} \quad \text{Eq. 1}$$

The equation for convective heating by the air is:

$$Q_{\text{air}} = M_{\text{air}} * C_p * (T_{\text{in}} - T_{\text{out}}) \quad \text{Eq. 2}$$

Where:  $Q_{\text{air}}$  = heat supplied by air, BTU/hr  
 $M_{\text{air}}$  = mass flow rate of air, lbs/hr  
 $C_p$  = heat capacity of air, BTU/lbs-°F = 0.249

The mass flow rate of air is given by the following equation:

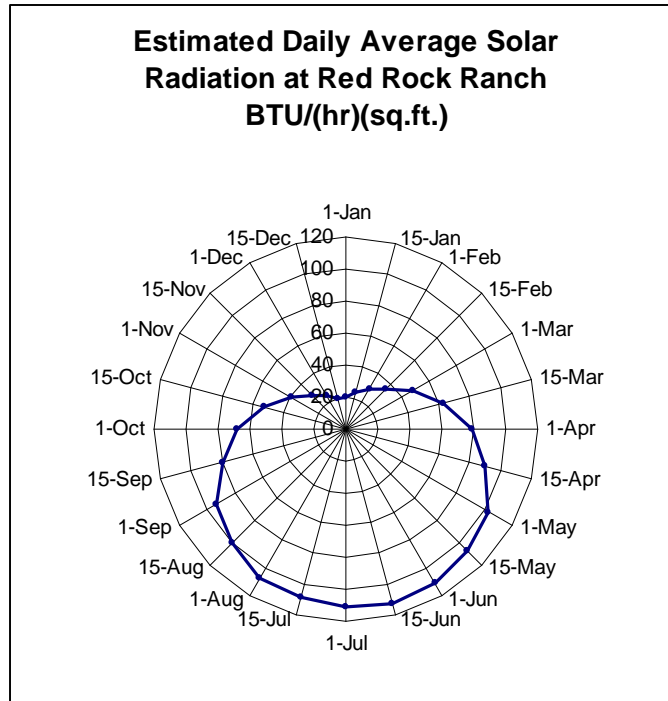
$$M_{\text{air}} = W_p * D_{\text{air}} * S_{\text{air}} * \rho_{\text{air}} \quad \text{Eq. 3}$$

Where:  $W_p$  = width of pond normal to wind direction, ft  
 $D_{\text{air}}$  = depth of air cooled by spray, ft  
 $S_{\text{air}}$  = speed of wind, ft/hr  
 $\rho_{\text{air}}$  = density of air, lbs/ft<sup>3</sup> = 0.0808 \* 459.7/( $T_{\text{in}}$  + 459.7)

Because of the need to minimize the wind drift of fine particulate pollutants (see Section 1.2), a fence has been installed around the spray pond to reduce the speed that air moves across the spray area. Assuming an air flow across the sprayed area of 2 miles per hour (average over a 24 hour day and assuming continuous spraying), a depth of affected air of 5 feet, and a width of 100 feet, 5.3 million cubic feet per hour (386,000 pounds per hour) of air would provide/absorb sensible heat. If we assume that this air were cooled an average 5°F (average over a 24 hour day), by providing heat to the evaporating water, then 386,000 BTU/hr would be provided by the air. This is enough heat to evaporate 1,056 gallons per day (0.73 gal/min) of water. Of course, if the spray is operated only a few minutes each hour, the heat supplied by air would be proportionally less.

I recommend that the appropriate air measurements be taken around the pilot spray pond at Red Rock Ranch so that the above estimates can be replaced with actual field measurements. Only by having actual measurements of the contribution of sensible heat by the air can the significance of this factor to evaporation be adequately assessed.

Solar radiation heat absorption is a function of the time of the year. This is shown in the figure below. This figure was determined by correcting the values in Table 12-5 in “Perry’s Chemical Engineers’ Handbook, 7<sup>th</sup> Edition” for the latitude of Red Rock Ranch (36° 25’), typical absorptivity of the rocks in the spray pond, and my estimate of typical values for the sun being obscured. These data and assumptions are shown in Appendix A.



With a peak daily average solar radiation absorption rate of 113 BTU/(hr)(ft<sup>2</sup>) and a 100 ft x 100 ft spray pond area, the maximum daily average heat absorption rate is 1.13 million BTU/hr. This is enough heat to evaporate 3,108 gallons per day (2.16 gal/min) of water.

The Stefan-Boltzmann equation for radiation heat loss is:

$$\Phi = \epsilon_{gr} \sigma A (T_{pond}^4 - T_{sky}^4) \quad \text{Eq. 4}$$

Where:  $\Phi$  = heat lost by radiation

$\epsilon_{gr}$  = emissivity of surface = estimated to be 0.3 for dry, salt covered rocks

$\sigma$  = Stefan-Boltzmann constant =  $1.74 \times 10^{-9}$  BTU/hr-ft<sup>2</sup>-°T<sup>4</sup>

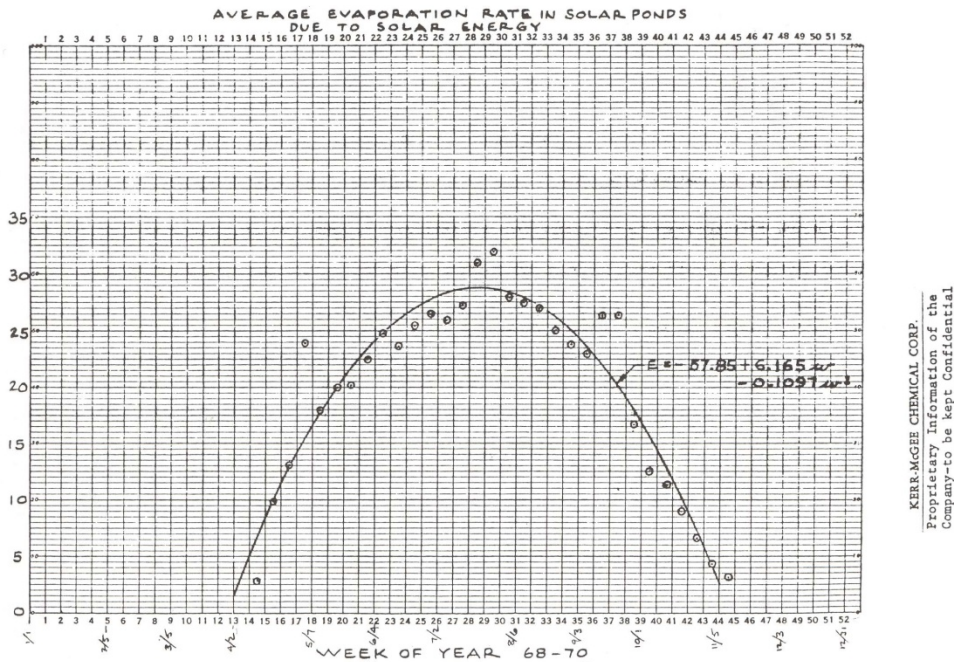
A = area of radiating surface, ft<sup>2</sup>

T = absolute temperature, degrees Rankine

In the summer, for an open surface pond with an area of 10,000 ft<sup>2</sup> (100 ft x 100 ft), an emissivity of 0.95 (a value suggested by the literature) and a water temperature of 85°F radiating to the sky with a temperature of -20°F, the radiation heat loss at night would be 837,000 BTU/hr. Each day of June has about 8 hours of dark night. During this time 6.7 million BTU would be lost. This is equivalent to losing 768 gallons per day through evaporation. But because the pilot test at Red Rock Ranch uses a spray pond, this heat loss is avoided because there is no open pond to reradiate heat to cool the water.

In the winter when the water temperature drops to about 45°F, about 454,000 BTU/hr would be lost from the pond. With 13 hours of darkness, 5.9 million BTU per day of heat would be lost. Again, because the pilot test at Red Rock Ranch uses a spray pond, this heat loss is avoided because there is no open pond to reradiate heat to cool the water.

Solar evaporation rates in Searles Valley have been measured for ponds that solar-concentrate brine that is saturated in sodium chloride (NaCl). The typical evaporation rates observed there are shown in the following graph. The total evaporation achievable there is typically 4,300 tons of water per acre per year.



Although the initial evaporation of drainage water at 1 wt% total dissolved solids will likely occur at a much higher rate than brine in Searles Valley, it will gradually fall as the NaCl and other dissolved solids concentrations rise. Once the water concentrates to near saturation with NaCl, the evaporation rates should be similar to those in Searles Valley. This fall in evaporation rate is the result of the decreasing equilibrium partial pressure of water above the elevated-TDS water. When the drainage water has been concentrated to NaCl saturation, the equilibrium partial pressure of water above the brine will be just 76% that of pure water, equivalent to a 9°F boiling point elevation.

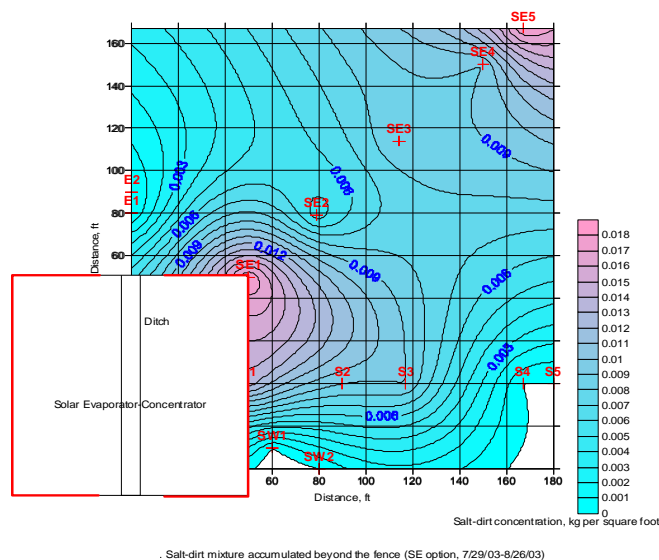
## 1.2 Air Quality - Particulate Emissions from Spray Evaporation Ponds

Rule 4202 of the San Joaquin Valley Unified Air Pollution Control District (APCD) regulates the emission of particulate matter (see Appendix B). This rule states that, "A person shall not discharge into the atmosphere from any source operation, particulate matter in excess of that allowed by the following process weight table." In Searles Valley, APCD regulations limit the emissions allowed from cooling towers. Since

cooling towers are very similar to spray ponds in that both disperse saline water into air, I would be very surprised if there were not similar regulations that apply to spray ponds in the San Joaquin Valley.

Data from Red Rock Ranch show that Sump D drainage water feeding the spray evaporator pond will contain about 750 metric tons (827 short tons) per year of total dissolved solids. Assuming that the water containing these solids must all be evaporated in the six summer months, the average solids operating rate during the summer will be 375 lbs/hr of solids. Since the pond would be operated for no more than 12 hours per day, the average hourly operating rate for the pond would be 750 lbs/hr of product. From a process standpoint, these solids would be taken as the product of the stationary, discharging process. The APCD table states that when the production rate is between 500 and 1,000 lbs/hr, the allowable emission rate is only 2.25 lbs/hr. This equates to about a maximum allowable loss of dissolved solids from the feed of about 0.30%.

Department of Water Resources (DWR) reports contain data, shown below, that show that the actual loss of salts from the spray pond is at least 10% and may be as high as 30%. One DWR report states that mist is indeed serious because the fence installed to control wind speed has been heavily coated with salt that originated as mist generated by spraying.



I am concerned that rule 4202 does apply to the spray pond. If this is the case and if the maximum allowable emission is as I suggested and the drift is as serious as indicated, then the present spray pond is very likely being operated in violation of APCD regulations. This possibility needs to be thoroughly investigated before proceeding with further testing of the spray evaporation pond concept.

Currently, the mist emissions are determined by placing weighed glass sheets at various locations downwind of the spray pond. After a measured period of time these plates are weighed again, and the difference between the initial and final weights is calculated. This difference is assumed to be the result of mist losses from the spray pond. The weakness

in this procedure is that part of the weight difference, perhaps even the majority, is the result of the accumulation of dust, not evaporated mist.

I suggest that the method to determine mist emissions be modified to measure mist alone. This would be done by placing clean glass plates as is presently done, but after exposure the plates would be washed thoroughly with demineralized water to remove all soluble salts. The wash water would be collected in a volumetric flask and the concentration of chloride in this water would be determined analytically. Then using the volume of water in the flask and the chloride concentration, the mass of chloride would be determined. Finally, using the chloride as a tracer, the total dissolved solids would be calculated, based on the ratio of total dissolved solids and chloride analyses of the water that was sprayed.

Inherent in spray ponds is the disbursement of water droplets into air. If it didn't do this, it wouldn't be a spray pond. But whenever water droplets are disbursed in air and the water in the droplets evaporates, discrete solid particles comprised of the dissolved solids are created. The only ways to avoid the production of these particulate emissions is to not spray water containing dissolved solids into the air or collect all of the mist before it leaves the spray pond area.

Mist eliminators provide a tortuous path for the exiting air to follow once it leaves the area where the mist is produced. The slatted fence surrounding the spray evaporation pond at Red Rock Ranch is presently acting like a mist eliminator, because salt builds up on the fence. But the single fence is a very inefficient mist eliminator because it offers a significant area without a tortuous path. In chemical plants a deep bed of wire mesh is often used to control mist, but this would be prohibitively expensive to surround a spray evaporation pond. A better choice would be install multiple, closely spaced, slatted fences around the spray pond, very close to the edge of the spray area. Probably four to six fences would be adequate, although this would have to be determined by testing. Also, these fences would have to either be tall enough so a strong wind could not carry the mist over the fence, or the sprays would have to be shut down whenever the wind exceeds a certain velocity. Again, testing is necessary to determine the relationship between the height of the fence and the allowable wind speed.

If a mist-control fence were installed, it would also be necessary to be able to collect the drainage water from the fence, including rain, and return it to the spray pond. This is because the fence will accumulate salt, and this cannot be allowed to return to the soil. Also, the fence will accumulate salt, which may require occasional washing of the fence with something like raw drainage water.

Mist-control fencing will have at least two negative consequences that will reduce spray pond capacity. One is that a mist-control fence will very likely reduce the flow of air across the spray area, and this will reduce the evaporation rate from the pond by reducing the sensible heat contribution of the air (see Section 1.1 above). Also, the fence will partially shade the spray area, further reducing evaporation.



All commercial solar evaporation operations I know of use surface ponds without spraying to enhance evaporation. This includes four facilities in California: the ponds in Searles Valley, the solar salt operations around San Francisco Bay, the salt ponds near Amboy, and the waste ponds of United States Borax in Boron. The California Department of Fish and Game (DFG) knows of the ponds in Searles Valley since it has required several mitigation measures to protect wildlife, yet these ponds are permitted by DFG. I see no good reason why a surface pond with proper wildlife mitigation would not be permitted by the DFG in the San Joaquin Valley.

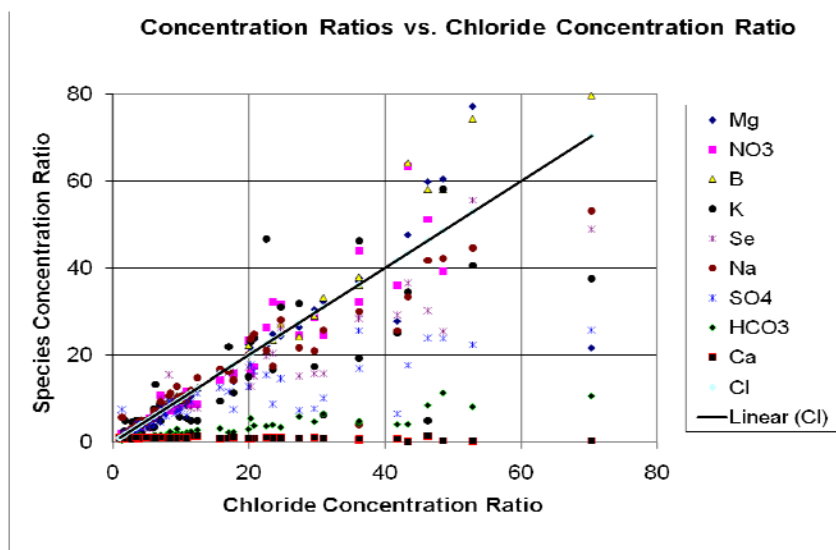
### 1.3 Brine Chemistry Description

#### 1.3.1 Concentration Ratios

The concentration ratio of a constituent is the concentration of that constituent in the concentrated water divided by the concentration of the same constituent in the feed water. Typically for solar ponds, concentration ratios would be calculated for all constituents that are present in significant concentrations.

Calculating and plotting concentration ratios is a convenient way to determine the points in an evaporation process where each constituent precipitates. Any constituent that is known to not precipitate can be used as the base for comparison of all of the other constituents. Once a constituent begins precipitating, its concentration ratio becomes lower than the ratios for those constituents that are not precipitating.

I have calculated the concentration ratios and plotted these in a graph for the Red Rock Ranch pilot spray pond tests in 2003 and 2004. This graph is shown below and in Appendix A. From these ratios it is clear that almost immediately upon concentrating, calcium and bicarbonate begin precipitating, since at even the lowest concentration ratios their ratios both fall way below the concentration ratio lines for chloride, nitrate and potassium. Once the sulfate concentration ratio increases to about 20, sulfate becomes a significant precipitate. However, up to the maximum concentration ratios in these tests, chloride, nitrate, boron and potassium do not precipitate.



### **1.3.2 Molarities, Molar Concentration Products and Weight Percents**

Chemical analyses can be used for other purposes besides following the progress of the concentration of the soluble species during evaporation. One purpose is to determine which compounds might precipitate because the concentrations in solution exceed saturation. This requires the molar concentration (moles per liter) of each of the ions to be calculated. To determine if a compound has reached saturation, the molar product for that compound is calculated, and this is compared to the molar product (known as solubility product) for that compound. If the actual molar product for a compound exceeds the solubility product for that compound, the water is supersaturated in that compound, and the compound will precipitate.

The molarities can also be used to estimate the relative amounts of material that will precipitate during evaporation. For example, the calcium concentration in Sump D water averages about 0.015 moles/liter, while sulfate averages about 0.045 moles/liter. If all of the calcium were to precipitate as gypsum (calcium sulfate dehydrate), then one third of the sulfate would be removed from the water as gypsum. Molar concentrations are also important when calculating material balances for the process.

Percentage concentrations are also important to calculate because percentages must be used to calculate material balances, and material balances are necessary to understand the concentration process. One of the most important percentages is that of water (H<sub>2</sub>O) in the concentrating drainage water, and to determine the percentage of water it is necessary to know weight of the sample. Weights can be obtained two ways, either by direct weighing of all of the samples prior to the analysis or by determining the specific gravity of the water. Of these, determining the specific gravity is the easiest since only one sample must be weighed, not all the samples. **Therefore, I very strongly recommend that for ALL future analyses, specific gravity of the water be added as one of the measurements.**

Pages 1-4 of Appendix A show the analyses for the Red Rock Ranch pilot tests. Included are the analyses in mg/L, concentration ratio, molarity in millimoles/L (1/1,000 of a mole per liter), weight percent (based on an estimated specific gravity derived from the total dissolved solids), and key molar products for the scale-forming compounds.

### **1.3.3 Brine Chemistry During Uncontrolled Brine Concentration**

#### **1.3.3.1 Precipitation of Calcium and Bicarbonate**

As shown above in the graph of concentration ratios, the precipitation of calcium and bicarbonate begins almost immediately after evaporation of the water begins. The bicarbonate precipitates only after it has decomposed to form carbonate, and it precipitates with calcium as calcium carbonate.

The equations below show the chain of chemical equilibria that carbon dioxide undergoes in solution as a function of solution pH.



When carbon dioxide is lost from Red Rock Ranch water, it is formed from two bicarbonate ions according to the following equation.



As can be readily seen, the loss of carbon dioxide results in an increase in the carbonate ion concentration in the water. And when the carbonate ion increases, the pH of the water increases. Also when the carbonate ion concentration increases, it is quickly precipitated as calcium carbonate by the calcium in the Red Rock Ranch water.

The carbonate equilibrium reactions have been extensively studied and equilibrium constants have been experimentally determined. The equilibrium equations are:

$$K_{\text{eq1}} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.16 \times 10^{-7} \quad \text{ref. 5} \quad \text{Eq. 7}$$

$$K_{\text{eq2}} = \frac{[\text{H}^+][\text{CO}_3^{=}] }{[\text{HCO}_3^-]} = 4.84 \times 10^{-11} \quad \text{ref. 5} \quad \text{Eq. 8}$$

Where:  $[\text{H}_2\text{CO}_3]$ ,  $[\text{H}^+]$ ,  $[\text{HCO}_3^-]$ , and  $[\text{CO}_3^{=}]$  are the respective molar concentrations of the various ions.

These equations allow the molar concentrations of the several carbonate species in the water to be calculated. For example, when the pH of the water is 7.6 and the bicarbonate ion concentration is .0022 molar (the conditions in RRR Sump D on 01/28/04), the hydrogen ion concentration is  $2.5 \times 10^{-8}$  molar (from the pH measurement), the carbonic acid ( $\text{H}_2\text{CO}_3$ ) concentration is  $1.3 \times 10^{-4}$  molar, and the  $[\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]$  ratio is 16.6. Also, the  $[\text{HCO}_3^-]/[\text{CO}_3^{=}]$  ratio is 519 and the carbonate ion concentration is  $4.3 \times 10^{-6}$  molar.

Another example, after the water has been concentrated by evaporation, is Tomato Tank 4 on 01/28/04. The pH of the water has increased to 8.4 by loss of carbon dioxide and the bicarbonate has been concentrated to .0050 molar. This has decreased hydrogen ion concentration to  $4.0 \times 10^{-9}$  molar, decreased the carbonic acid ( $\text{H}_2\text{CO}_3$ ) concentration by 2/3 to  $4.7 \times 10^{-5}$  molar, and increased the  $[\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]$  ratio to 104. Also, the  $[\text{HCO}_3^-]/[\text{CO}_3^{=}]$  ratio has decreased to 82 and the carbonate ion concentration has increased 14-fold to  $6.0 \times 10^{-5}$  molar.

In the analyses of water from the pilot test at Red Rock Ranch, the concentration of bicarbonate in the water is seen to increase very regularly, although slowly, with increasing total dissolved solids (see graph above). This increase occurs even though bicarbonate is both decomposing and precipitating as calcium carbonate.

The carbonic acid ( $\text{H}_2\text{CO}_3$ ) concentration decreases rapidly as the pH of the water increases, as can be seen from Eq. 7. As the carbonic acid concentration decreases, the rate of loss of carbon dioxide from the water decreases. Somewhat surprising is the fact that the carbonic acid ( $\text{H}_2\text{CO}_3$ ) concentration is only very weakly influenced by an increase in total dissolved solids (see graph in Appendix A).

Even more surprising is the fact that bicarbonate increases in the concentrating water even though the calcium is present in the sump D water at a molar concentration about five times higher than the bicarbonate. If half of the bicarbonate is lost by carbon dioxide evolution to produce carbonate, the bicarbonate is present at just 1/10 the amount needed to precipitate all the calcium. Yet bicarbonate concentrates in the water.

Because calcium carbonate is precipitating from the concentrating water, it is at least saturated in the water. Because it is precipitating, we can use a predictable formula known as the solubility product to understand the precipitation. This formula is:

$$K_{sp} = [\text{Ca}^{+2}][\text{CO}_3^{-}] = 4.7 \times 10^{-9} \quad \text{ref. 5} \quad \text{Eq. 9}$$

This equation predicts that when the calcium concentration is 0.0142 molar, the average of all calcium analyses, the carbonate concentration will be  $3.3 \times 10^{-7}$  molar at saturation. When looking at the actual analytical data for the Catch Basin at Red Rock Ranch on 31 August 2004, we find that the calcium is 0.0148 molar and the carbonate is  $4.2 \times 10^{-5}$ , or over 100 times higher than predicted by the solubility product. This shows that the water is actually substantially supersaturated in calcium carbonate. Further evidence that calcium carbonate is supersaturated is the average product of calcium and carbonate molarities. This is  $4 \times 10^{-7}$ , almost 100 times the solubility product for calcium carbonate. Therefore, calcium carbonate is expected to precipitate and coat all equipment in the spray-evaporation system.

### **1.3.3.2 Precipitation of Calcium Sulfate**

The calcium concentration remains practically unchanged through most of the evaporation-concentration process (see concentration ratio graph above). Only when the sulfate concentration exceeds 0.7 molar (about 5.5 wt%) does the calcium significantly fall below a range of  $0.014 \pm 0.004$  molar. Because the bicarbonate molarity in the sump D water is just 1/5 the molarity of calcium, the calcium concentration must be held down during evaporation by something in addition to calcium carbonate precipitation. This second precipitate is gypsum (calcium sulfate dihydrate).

The solubility product for gypsum is:

$$K_{sp} = [\text{Ca}^{+2}][\text{SO}_4^{-}] = 2.4 \times 10^{-5} \quad \text{ref. 5} \quad \text{Eq. 10}$$

Evidence that gypsum is supersaturated is the average product of calcium and sulfate molarities. This is  $2.7 \times 10^{-3}$ , almost 100 times the solubility product for gypsum.

Therefore, gypsum is also expected to precipitate and coat all equipment in the spray-evaporation system during the entire sequence of concentration.

The molar concentration of calcium is about 1/3 the sulfate concentration. This means that about 1/3 of the sulfate present in the Red Rock Ranch drainage water will be precipitated as gypsum. In the summer, enough gypsum precipitates to allow 95% of the water in the drainage to be evaporated without sodium sulfate crystallization. Even though Glauber's salt (sodium sulfate decahydrate) has a relative low solubility at low winter temperatures, the pilot test data suggest that gypsum precipitation will still remove enough sulfate to allow more than 90% of the water to be evaporated from the drainage water before Glauber's salt crystallizes.

Only after all of the calcium has precipitated will the sulfate concentration rise high enough to allow sodium sulfate to crystallize.

#### **1.3.3.3 Precipitation of Sodium Sulfate**

Sodium sulfate is the third constituent to precipitate when Red Rock Ranch water is concentrated by solar evaporation. This occurs when the sulfate concentration rises to over 3 wt% in the winter and 5 wt% in the summer. During cold weather (late October through mid April) sodium sulfate crystallizes as Glauber's salt (sodium sulfate decahydrate). This can only occur after more than 90% of the water in the Red Rock Ranch drainage water has been evaporated. Also, Glauber's salt will only crystallize when the water temperature is below about 60°F, as Glauber's salt solubility falls rapidly when the temperature falls below 60°F.

During the warmer month (late April through early October) anhydrous sodium sulfate is the sulfate material that crystallizes. Because of the higher solubility of anhydrous sodium sulfate at higher temperatures, the drainage must be evaporated further to induce sodium sulfate to crystallize.

#### **1.3.3.4 Disposition of Selenium**

The data on selenium are somewhat confusing. The concentration ratios for selenium suggest that it crystallizes, but these ratios cannot be determined with certainty because the selenium concentrations in the drainage water are very low, which makes quantitative analyses of the water imprecise. The disposition of selenium can probably be determined by analyzing the precipitated gypsum scale for selenium. If selenium precipitates, it should be found at a high concentration in the gypsum scale.

#### **1.3.3.5 Non-precipitating Constituents**

During the spray-evaporation pilot tests of Red Rock Ranch drainage water, chloride, nitrate, boric acid, potassium and magnesium did not precipitate. It does appear that in one test, 27 Sept 2004 in Tomato Tank 3, sodium chloride was very close to saturation. This occurred after about 98% of the water had been evaporated from the drainage water.

The concentrated water has an unusual and complex composition. This can best be seen from the analysis of the water in Tomato Tank 3 on 27 Sept 2004. This water contains about 16 wt% sodium chloride, 9 wt% sodium sulfate, 3 wt% sodium nitrate, 1.1 wt% magnesium chloride, 0.6 wt% boric acid, and 0.17 wt% sodium bicarbonate. All other constituents are present at negligible concentrations.

#### **1.4 Analyses to Use for Control During Solar Evaporation**

##### **1.4.1 Conductivity vs. Water Composition**

It appears that conductivity is being used to estimate the quantity of dissolved solids in the water as it concentrates. Theoretically, solution ionic strength should be the parameter that is best estimated by conductivity since this is a measure of the electronic charge of the solute ions that produce the conductivity. Ionic strength is the sum over all ions of the products of molarity and ionic charge. For example, a 1.0 molar solution of sodium chloride would have an ionic strength of 2 ( $\text{Na} = 1.0 \times 1 = 1.0$ ,  $\text{Cl} = 1.0 \times 1 = 1.0$ ). A 1.0 molar solution of magnesium chloride would have an ionic strength of 4.0 ( $\text{Mg} = 1.0 \times 2 = 2.0$ ,  $\text{Cl} = 2.0 \times 1 = 2.0$ ). The units are charge equivalents per liter.

I have plotted conductivity for all the Red Rock Ranch pilot test data versus both ionic strength and total dissolved solids. These plots are shown in Appendix A. From these plots it is clear that ionic strength actually correlates better to conductivity than total dissolved solids. This is especially true when the conductivity is below 100,000  $\mu\text{S}/\text{cm}$ .

These conductance plots also show that the conductivity measurement becomes much more scattered at high conductance. This is likely the result of electrode overload at high ionic strength.

##### **1.4.2 Specific Gravity vs. Water Composition**

Normal industrial practice for field control of solar ponds systems is to use specific gravity to track total dissolved solids once the solution is sufficiently concentrated. For the concentrated agricultural drainage water, this threshold appears to be at about 6 wt % total dissolved solids. I suggest that field control of the pilot tests use specific gravity in the future once the conductivity reaches 60,000  $\mu\text{S}/\text{cm}$ .

A second reason for measuring specific gravity is that it allows solute concentrations to be determined in weight percents. This is important because weight percents are needed to be able to calculate mass balances, and mass balances are necessary to make process design calculations for the complex separation processes needed to recover pure products from concentrated drainage water.

#### **1.5 Analyses of Minor Constituents**

##### **1.5.1 Strontium and Barium**

Solar-concentrated Red Rock Ranch drainage water contains from 0.1 to 0.4 molar sulfate and also a small amount of carbonate from bicarbonate decomposition. As can be seen from the solubility products shown below, the sulfate and carbonate salts of

strontium and barium are nearly insoluble in drainage water. Therefore, both alkaline earth metals will be absent from concentrated Red Rock Ranch drainage water. Because of this, during future pilot tests there should be no need to analyze for these elements.

#### Strontium Sulfate

$$K_{sp} = [Sr^{+2}][SO_4^{=}] = 7.64 \times 10^{-7} \quad \text{ref. 5} \quad \text{Eq. 11}$$

#### Strontium Carbonate

$$K_{sp} = [Sr^{+2}][CO_3^{=}] = 7 \times 10^{-10} \quad \text{ref. 5} \quad \text{Eq. 12}$$

#### Barium Sulfate

$$K_{sp} = [Ba^{+2}][SO_4^{=}] = 1.6 \times 10^{-9} \quad \text{ref. 5} \quad \text{Eq. 13}$$

#### Barium Carbonate

$$K_{sp} = [Ba^{+2}][CO_3^{=}] = 1.5 \times 10^{-9} \quad \text{ref. 5} \quad \text{Eq. 14}$$

### **1.5.2 Aluminum and Silica**

Silica is expected to be present in the drainage water at low concentrations because the water contains around 600 mg/L of calcium. The high calcium will precipitate silica as insoluble calcium silicate during evaporation. As such, it will simply join the calcium carbonate and gypsum scale formed as the water concentrates. Sump D water was the only sample analyzed for silica. There, silica was about 30 mg/L. At this concentration calcium silicate will constitute approximately 5.6% of the total scale formed during evaporation. It should be noted that calcium silicate scale cannot be removed by any chemical method. Only mechanical removal works for calcium silicate scale.

If calcium is removed prior to evaporation, silica will tend to concentrate in the water during evaporation. At some point it will become saturated, but I don't know when that will occur.

Aluminum appears to be insoluble in the drainage water. In most samples it was below the reporting limit for the analytical procedure. However, aluminum was quantified in set of samples taken on 28 October 2003. From this limited data it appears that aluminum also precipitates during evaporation, and in doing so, joins the calcium scale. The form of the scale is unknown, but it is most likely insoluble calcium aluminate scale.

### **1.5.3 Copper, Manganese, Molybdenum and Vanadium**

Copper was analytically quantified in a set of samples taken on 28 October 2003. Even then it did not appear that copper concentrated in the water. Instead, it precipitated to join the scale. Even if copper did tend to concentrate, it would be very easy to control by simply adding a very small amount of sodium sulfide. This would precipitate the copper as cupric sulfide, an extremely insoluble material ( $K_{sp} = 8 \times 10^{-37}$ ). At most only occasional analytical spot checks on copper appear necessary in the future. These spot checks should be on the most concentrated water.

Manganese was above the analytical reporting limit for only 7 of the 98 samples analyzed, and only one of the seven was more than twice the reporting limit for the analytical procedure. Furthermore, the analyses of concentrated water showed no indication that manganese concentrates during evaporation. Thus, it looks like it should no longer be necessary to analyze for this metal.

Molybdenum was reported only twice, and both results were at or below the stated analytical reporting limit. No analytical results of concentrated water were available, so it is uncertain whether or not molybdenum concentrates during evaporation. I suggest that at least one series of analyses be done for the concentrated brine to determine if molybdenum concentrates during evaporation.

Vanadium was always reported as being below the analytical reporting limit. No analyses of concentrated water were available so it is uncertain whether or not vanadium concentrates during evaporation. I suggest that at least one series of analyses be done for the concentrated brine to determine if vanadium concentrates during evaporation.

#### **1.5.4 Dissolved Organic Carbon**

Dissolved organic carbon is a potentially important player in brine evaporation. This is because some organic compounds are strong crystal-habit modifiers that can change the course of crystallization. However, crystal-habit modification is totally dependent on the organic compound, with crystal habit only modified by that compound. At this time, I believe that it would be prudent to at least analyze for total organic carbon during the evaporation process to determine if the organic carbon concentrates.

### **2.0 Proposed Control of Brine Chemistry During Evaporation**

#### **2.1 Control of Scaling in the Evaporator**

At 600 mg/L calcium, the agricultural drainage water as measured by Sump D water composition contains over 2,000 mg/L of potential scale material. Since the Sump D water contains just 11,000 mg/L total dissolved solids, scale-forming constituents comprise over 18% of the total dissolved solids in the water. When processing water this high-scaling water, scaling of the spray-evaporator will likely be a serious impediment to achieving low cost operation; when scale deposits reach a sufficient thickness, they will plug the spray rock bed, piping, pump, and especially the spray nozzles. While in some cases these can be cleaned using chemical treatments, often it will require replacing the plugged equipment.

Both potential scale materials are calcium salts: calcium carbonate and gypsum (calcium sulfate dihydrate). Uncontrolled, the scale deposited will be about 90% gypsum and 10% calcium carbonate. Of these two, only calcium carbonate can be removed by chemical means. This can be done using a dilute solution of hydrochloric acid. Calcium sulfate is not reactive with either acids or bases, although it will react slowly with a soda ash (sodium carbonate) solution to re-precipitate as calcium carbonate, which can then be



removed with dilute acid. The more common way to deal with gypsum scale is to remove it mechanically.

If remedial removal of scale or equipment replacement is undesirable, it will be necessary to prevent scale deposition. Calcium carbonate scale can be prevented two ways. One is to acidify the water to destroy the bicarbonate and evolve all of the carbon dioxide. This will require adding enough strong acid (sulfuric or hydrochloric acid) to lower the pH to about 5.0. Then when this acidic water is sprayed to evaporate water, the carbon dioxide will be released. When the Sump D water contains 300 mg/L of bicarbonate (as  $\text{CaCO}_3$ ), typical for this water, about 145 mg/L of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) or 110 mg/L of hydrochloric acid (HCl) will be required. If sulfuric acid at a cost of \$50 per ton is used, acid treatment will cost \$9.83 per acre-foot of water for only that reagent. This treatment, however, will leave all the calcium in the drainage water where it will simply precipitate as gypsum as water is evaporated.

A second way to prevent calcium carbonate scale is to precipitate the calcium carbonate in a tank (or pond) before the drainage water is fed to the spray evaporator. This would require mixing enough sodium hydroxide into the drainage in the feed to the tank to raise the pH to about 9.2. This will convert all of the bicarbonate to carbonate which will then precipitate in the tank as calcium carbonate. When the Sump D water contains 300 mg/L of bicarbonate (as  $\text{CaCO}_3$ ), typical for this water, about 120 mg of caustic soda (sodium hydroxide/ $\text{NaOH}$ ) will be required per liter of water. If caustic soda costs \$150 per ton, caustic soda treatment will cost \$24.40 per acre-foot of water for only that reagent. This treatment will remove the calcium precipitated from the drainage water so that it cannot precipitate as gypsum as water is evaporated. However, about 80% of the calcium originally present will still remain in the water where it can precipitate as gypsum.

Hydrated lime could also be used to raise the pH of the drainage water. The problem with using lime is that it adds calcium to the water instead of removing calcium. The consequence of using lime would be a reduction in calcium carbonate scale but only at the cost of an increase in gypsum scale.

Although calcium carbonate can be easily controlled, it is not the most serious scale component. This is gypsum (calcium sulfate dihydrate) since it constitutes about 90% of the total scale. The only way to positively prevent gypsum scale is to remove all calcium from the drainage water fed to the spray evaporator. This can be done two ways: ion exchange and chemical precipitation. Of these, chemical precipitation has lower costs.

Chemical precipitation of all calcium from the drainage water will require two reagents, caustic soda (sodium hydroxide/ $\text{NaOH}$ ) and soda ash (sodium carbonate/ $\text{Na}_2\text{CO}_3$ ). The caustic soda (at a cost of \$24.40 per acre-foot of water) converts the bicarbonate in the drainage water to carbonate so that it can precipitate part of the calcium as calcium carbonate. Then additional carbonate is added, in the form of soda ash, to precipitate the remaining calcium as calcium carbonate. The amount of soda ash required would be about 636 mg per liter of water. If soda ash costs \$85 per ton, soda ash treatment will cost \$73.30 per acre-foot of water. This will bring the total cost for reagents for calcium removal to \$97.70 per acre-foot of water. The calcium carbonate would have to be

filtered out of the water prior to the water being fed to the spray evaporator. If this were not done, calcium carbonate would eventually fill the void space in the rocks in the evaporator, thereby reducing evaporator effectiveness.

Precipitated calcium carbonate can be a valuable product if it can be used as filler in the wood pulp used to make paper. But this requires precipitation to be done in such a way that the correct physical and chemical properties of the material are produced. Although I am aware of this market, I do not know the conditions necessary to make the required product. I do know that the precipitated calcium carbonate must be very fine, only 1 to 2 microns in size.

## **2.2     Calcium Removal at Minimum Reagent Cost**

If the costs of dealing with scaling are lower than the cost of reagents to totally prevent scaling, there is an alternate way to remove all of the calcium from the brine. This is to precipitate calcium as gypsum during evaporation until the  $[\text{HCO}_3^-]/[\text{Ca}^{+2}]$  molar ratio in the concentrated brine equals about 1.0. This will likely remove about 97% of the calcium as gypsum without the need to purchase reagents.

At this point caustic soda would be added to convert the remaining bicarbonate into carbonate which would then precipitate all of the remaining calcium. Only the residual calcium would require the use of a reagent to reduce calcium to zero, and this would only be enough caustic soda to convert the bicarbonate to carbonate. At this point, treatment with caustic soda will require 18 mg of caustic soda per liter of Sump D water. At a caustic soda cost of \$150 per ton, the caustic soda reagent will cost about \$3.66 per acre-foot of Sump D water. As with the more extensive use of reagents, it will be necessary to filter the precipitated calcium carbonate prior to returning the water to the spray evaporator.

The precipitation of calcium as gypsum will also remove more than 25% of the sulfate as calcium sulfate in the drainage water, thereby reducing the amount of sodium sulfate that must be recovered.

If the decision is made to allow most of the calcium to precipitate during solar evaporation, I strongly recommend that this evaporation occur in a static solar pond (one without water sprays). This will allow the precipitated calcium scale to largely settle to the bottom of the pond where it will cause few or no operating problems. If a spray pond is used, the calcium scale will certainly result in costly maintenance of the circulation pump, water piping and the sprays.

## **2.3     Control of Sodium Sulfate Crystallization - Summer**

Although a small amount of evaporation will be possible in the winter, 90% or more of the evaporation of drainage water will occur in the summer when the days are long, the sun is high in the sky, and the air is warm. This means that summer will be the only time of the year when enough volume of feed will be available for the recovery of significant quantities of the very soluble constituents.

The recovery of the soluble constituents will first require the drainage water to be evaporated until it is nearly saturated in sodium sulfate. On cooling of this concentrated water to 0 to 5°C, the only compound that will crystallize is Glauber's salt (sodium sulfate decahydrate). The chloride and nitrate salts of sodium and magnesium all are more soluble at 0 to 5°C than Glauber's salt at the concentrations present in the concentrated water. Since the crystallization of Glauber's salt will require the concentrated water to be cooled to about 0 to 5°C in the summer, artificial refrigeration will be required.

If the concentrated water is free of insoluble impurities such as dust, it will be possible to produce pure, salable quality, anhydrous sodium sulfate product from the Glauber's salt crystallized by the cooling. However, to make salable anhydrous sodium sulfate, a full chemical plant will be required. This plant would include: feed water filtration to ensure feed that is free of insoluble impurities, a refrigerated Glauber's salt crystallizer and filter to separate the pure crystals from the residual brine, an evaporator to remove the water of hydration in the Glauber's salt crystals, a sodium sulfate centrifuge and dryer, and product storage and shipping facilities. This will require considerable capital and significant operating costs. It is beyond the scope of the current project to design such a plant and estimate the associated costs.

#### **2.4 Control of Sodium Sulfate Crystallization - Winter**

In theory at least, it would be possible to use natural cooling in the winter to cool the concentrated brine to crystallize Glauber's salt. Practically speaking, this may not be possible because it may not be feasible to store the huge quantity of summer-enriched brine except in a large, open basins or a large storage tank.

Of the 827 tons per year of total dissolved solids in the drainage water, about 400 tons would be sodium sulfate. Assuming that the concentrated brine in the summer contains 8.0 wt% sodium sulfate, and that the concentration can be lowered to 3.5 wt% on cooling, it would be necessary to store about 9,000 tons of brine. Assuming a specific gravity of 1.3, the volume of solar concentrated brine that would have to be stored for up to three months (from October until January) is 1.65 million gallons or 5.1 acre-feet. If this were stored in a tank, the tank would need to be about 100 feet in diameter and 25 feet deep. If a double-lined pond were used, it would be 100 feet square by 20 feet deep.

A second tank vessel (tank or double-lined pond), nearly as large as the feed brine vessel, would be required to hold the discharge brine from the natural cooling process. This is because after the brine has been cooled, the Glauber's salt and the brine must be separated before the brine warms since the warmer brine will simply re-dissolve the Glauber's salt if they are left together. Also, the brine after Glauber's salt crystallization is still saturated with salts and must be processed further for the recovery of these salts, most likely involving additional solar evaporation the following summer.

Once natural cooling had been used to crystallize the Glauber's salt, the Glauber's salt will have to be recovered and processed further if salable sodium sulfate, or a derivative product, is to be produced.

## **2.5     Separation of Boric Acid**

Following the crystallization of Glauber's salt, the resultant brine contains a complex mixture of sodium and magnesium salts of chloride and nitrates, as well as boric acid. Separating this complex mixture will be difficult at best. The first step would be to use solvent extraction to remove the boric acid. The solvent loaded with boric acid would be further processed to recover boric acid as a salable quality product. Various solvents are feasible and are described in the literature. It is beyond the scope of the current project to design a plant to recover boric acid and estimate the associated costs.

## **2.6     Separation of Magnesium Oxide**

The next step would be to add caustic soda (sodium hydroxide/NaOH) to precipitate the magnesium as magnesium hydroxide  $[\text{Mg}(\text{OH})_2]$ . This would be filtered and washed on the filter to remove all entrained brine to remove all sodium salts. Finally, the filter cake would be calcined to magnesia (magnesium oxide/MgO). If processed properly, the magnesia should be a salable quality product. It is beyond the scope of the current project to design a plant to recover magnesia and estimate the associated costs.

## **2.7     Separation of Sodium Chloride and Potassium Nitrate**

After magnesium hydroxide precipitation, the brine would return to the solar evaporator to continue concentration. During this step sodium chloride would crystallize in the solar evaporator. Evaporation would continue until the brine is nearly saturated in sodium nitrate. The initial sodium chloride crystallized should be sufficiently pure to be salable. But during the later stages of evaporation the salt will likely become contaminated with sodium sulfate.

The final step would be to heat the brine to near boiling and add potassium chloride to the brine to produce a solution of potassium nitrate and sodium chloride. The brine would be evaporated hot (around 210°F) where sodium chloride would continue to crystallize while the potassium nitrate concentrates in solution. The sodium chloride would be centrifuged and dried to make additional salable quality sodium chloride.

Once potassium nitrate reaches saturation in the hot brine, the brine would be cooled to about 5°C to crystallize potassium nitrate. It is possible that the potassium nitrate would be contaminated with glaserite [sodium-tripotassium sulfate/  $\text{NaK}_3(\text{SO}_4)_2$ ]. This salt mixture would be centrifuged and dried to make a potassium-nitrate-sulfate fertilizer that is chloride free and low in sodium for reapplication to the fields. The residual brine from potassium-nitrate-sulfate crystallization would be recycled to the sodium chloride evaporator for further recovery of sodium chloride and potassium nitrate.

It is beyond the scope of the current project to design an evaporator-crystallizer plant to recover sodium chloride and potassium-nitrate-sulfate and estimate the associated costs.

## **2.8     Residual Brine**

Selenium and other minor impurities will continue to concentrate in the recycling brine in the sodium chloride/potassium nitrate process. To remove these impurities it will be necessary to bleed part of the potassium nitrate mother liquor to remove them. It will likely be necessary to dispose of this small volume of brine as hazardous waste because the quantities of potentially recoverable materials are too low to make their recovery economical.

## **3.0     Possible Uses of Intermediate Brine and Sodium Sulfate Product**

### **3.1     Solar Gradient Pond for Electric Power Generation**

The density gradient solar power generation pond is technology that was developed more than 50 years ago but has not yet achieved widespread application. The University of Texas at El Paso has an active program to improve this technology to make it more competitive in today's energy market. DWR should maintain active contact with that project so that it can be in a position to assist the commercialization of the technology if it becomes economic.

The brine that can be produced from agricultural drainage water would be well suited for use in a density gradient solar power generation pond. The unique combination of sodium and magnesium salts of chloride, nitrate and sulfate should be able to produce very high-density brine when concentrated to near saturation. It should also be possible to increase this density further by saturating these brines with selected solids, if necessary.

A density gradient solar power generation pond will have an efficiency of 10% or less in converting the collected thermal energy into electricity. The remaining 90% of the thermal energy will have to be rejected as waste heat. Typically this would be done using a cooling tower, but a spray evaporation pond could also be used. Both the cooling tower and the spray pond will consume a large volume of water through evaporation.

It would certainly be beneficial to use the waste heat from a power generation system to evaporate waste agricultural drainage water. In theory, this could be done by circulating concentrating drainage water between the condenser for the power generation turbine and the cooling tower or evaporation pond. The turbine condenser would warm the water, and the warm water would then be cooled by evaporation in the cooling tower or evaporation pond before subsequent reheating in the turbine condenser.

The major problem with using untreated agricultural drainage water in a turbine condenser is that it will deposit a thick gypsum scale on the condenser tubes. This will require frequent major maintenance of the condenser and that will require considerable down-time for the generator. Of course gypsum scale can be prevented by first removing

all of the calcium before using the water in the turbine condenser system. Calcium removal would be done as described above.

Spray evaporation of agricultural drainage water is being proposed, apparently because the DFG has said it will not accept surface ponding of water. Although the surface water will be low in total dissolved solids in a solar gradient pond, at least relative to the water at the bottom of the solar gradient pond, I still see the proposal to use solar gradient ponds for power generation as being in conflict with the DFG ban on surface ponding of agricultural water. This is because the surface water in a gradient pond may still contain substantial concentrations of the constituents that are of concern to the DFG. Before proceeding further with solar gradient ponds, I suggest that the acceptability of these ponds to the DFG be determined.

### **3.2 Traditional Sodium Sulfate Market**

The status of the traditional United States sodium sulfate market is followed monthly by Dennis Kostick of the United States Geological Survey (USGS). For the five-year period, 1999-2003, domestic consumption of sodium sulfate averaged 418,000 tons per year. In 2003, domestic consumption was 405,000 tons. In addition to domestic markets, sodium sulfate manufacturers were also able to export an average of 154,000 tons per year in the same five-year period. See Reference B-7 for the 2004 USGS report on sodium sulfate.

Two companies produced sodium sulfate from mined natural sources in 2003, and 15 companies produced byproduct sodium sulfate for sale as part of other processes. Some of the other processes that make byproduct sodium sulfate are: battery reclamation and the production of ascorbic acid, cellulose, rayon, and silica pigments.

It will be very difficult to penetrate the current market with new, large-scale production because of the strength of the current manufacturers. One existing California natural sodium sulfate manufacturer is very large, producing nearly half of the total domestic production. In addition, it has reserves that can support the current production rate for more than 2,000 years. The plant is also fully integrated with other manufacturing facilities, and it is fully depreciated. Similarly, it will not be possible to displace the byproduct sodium sulfate, because the producers consider sodium sulfate to be more of a disposal problem than a product.

### **3.3 Other Possible Uses for Sodium Sulfate**

It is technically feasible to convert sodium sulfate to other products, but in today's economy none of these has been economically feasible. Three such processes are discussed below.

#### **3.3.1 Electrolysis to Produce NaOH and H<sub>2</sub>SO<sub>4</sub>**

The process to electrolyze sodium sulfate is analogous to the electrolysis of sodium chloride except that sulfuric acid would be produced instead of chlorine gas. Both

processes would use similar electrolytic cells, both would use approximately the same amount of electricity, and both should produce the same strength of caustic soda leaving the cells. The main differences are in raw materials costs and coproduct values. Because of the similarities between the processes, we can assess the relative economics of both processes by considering just the major differences.

In a caustic-chlorine plant, for every ton of chlorine produced, 1.1 tons of caustic soda would be produced. The sum of these is commonly called an “electrochemical unit” (ECU). For a sodium sulfate electrolysis plant, the ECU would be 1.1 tons of caustic soda and 1.226 tons of sulfuric acid.

On a sodium basis, both electrolytic processes would use about the same amount of electricity (3.2MW-hr per ECU). Typically, the cost of electricity at most caustic-chlorine plants is very low, because they have invariably been constructed where there is low-cost electricity. In contrast, California has the highest electricity costs in the United States, about \$45 per MW-hr (\$144 per ECU) for base-load industrial users. This means that any electrolytic plant built in California will have up to a \$70 per ECU economic disadvantage compared to plants built in other states where power prices could be half those in California.

The feed to an electrolytic process to convert sodium sulfate to caustic soda (NaOH) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) would be melted Glauber’s salt; there would be no need to start with dry anhydrous sulfate. Using melted Glauber’s salt will at least reduce the cost of the sodium sulfate raw material by avoiding the energy-intensive evaporation and drying steps. Still, most sodium chloride for caustic-chlorine production is solution mined from thick salt beds that are very close to the plant, and this supplies salt at a very low cost. This results in a lower raw material cost for chlorine than for sulfuric acid.

A market assessment of caustic soda and chlorine is shown in Reference B-9 titled, “Chlorine: World Outlook.” Although dated, the market fundamentals are still generally valid. Caustic soda and chlorine prices tend vary inversely with each other. When the caustic price is high, the chlorine price is low, and when caustic price is low, the chlorine price is high. More nearly constant is the price for an electrochemical unit (ECU). (An ECU is the total of price of one ton of chlorine plus 1.1 tons of caustic soda.) The more stable ECU price is because both commodities are produced together at the ratio of 1.1 tons of caustic soda per ton of chlorine, and there is little storage capacity for either product. Therefore, when the demand for one is higher than the other, the high demand product is in short supply while the other product is in surplus. When this happens, normal supply/demand pricing occurs; the price of the product in short supply will increase while the price of the product in surplus falls.

Sulfuric acid is presently produced as either a single product by burning elemental sulfur or hydrogen sulfide, or as a byproduct of other operations. One major source of byproduct sulfuric acid is the copper smelting process. While byproduct sulfuric acid has to be sold regardless of price, not enough is produced to satisfy the total demand. That which is produced as a single product must be profitable; otherwise it would not be produced. Because of these supply factors, the price for sulfuric acid is much more stable

than chlorine, set by the need for the single products plants to be profitable yet offer a competitive price. Currently, the price for sulfuric acid is about \$50 per ton.

These marketing factors strongly influence the economics of a process producing caustic soda and sulfuric acid from sodium sulfate. When caustic soda prices are high (caustic is in short supply), the electrolysis of sodium sulfate might be economic. But when caustic prices are low, like in 1994 when the caustic price dropped to as low as \$50 per ton, the market value of one ECU would be just \$116. At this ECU value, caustic soda and sulfuric acid products would not support even the cost of the electricity to make them, much less the other operating costs and capital charges.

If it is assumed that in California the cost of electricity at \$144 per ECU were half the total manufacturing cost, and if the market value of sulfuric acid were \$50 per ton, the market value of the caustic soda would have to be at least \$216 per ton. For the time period 1987 through 1998, this pricing for caustic was achieved less than 1/3 of the time. Given these economic factors it is highly unlikely that the electrolysis of sodium sulfate in California will be an economic alternative.

### **3.3.2 React with $\text{NH}_3$ and $\text{CO}_2$ to Make $(\text{NH}_4)_2\text{SO}_4$ and $\text{Na}_2\text{CO}_3$**

In the 19<sup>th</sup> century a process was developed to make “synthetic” soda ash ( $\text{Na}_2\text{CO}_3$ ) and byproduct calcium chloride from sodium chloride and limestone. This process is widely known as the Solvay process, named after the company that first developed the process. Even today, more than half of the world’s production of soda ash is made using this process.

I am aware of one variation on the Solvay process that has been developed through commercialization in Japan. In this process, sodium chloride, ammonia and carbon dioxide are used to make the coproducts of soda ash and ammonium chloride. About seven years ago this plant was forced to shut down because it was no longer economic.

In theory, at least, it should be possible develop a similar variation on the Solvay process where sodium sulfate, ammonia, and carbon dioxide would be used to produce soda ash and ammonium sulfate. However, to date, this has not been practiced commercially anywhere in the world. Considerable process development would be required to even evaluate the technical feasibility of this process.

Important economic factors to be considered in this process are the cost of raw material (specifically sodium sulfate, ammonia, carbon dioxide, thermal heat, and electricity) and the value of the products.

Considering first the value of the products, soda ash is a major industrial commodity that is used primarily in the manufacture of glass. It also is used as an alkali raw material in markets that may also be supplied by caustic soda. All soda ash consumed in the United States is derived from mined trona ( $\text{Na}_2\text{CO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ) and is, thus, considered natural soda ash. About 90% is produced in Green River, Wyoming, and the remainder is produced in Searles Valley, California. Typical manufacturing costs for natural soda ash



are from \$50 to \$60 per ton. The average net back price to the plants is about \$75 per ton.

Although I believe that others associated with this project have a better understanding of the ammonium sulfate market, I will also make a few comments about this product. The value of ammonium sulfate is in the nitrogen; the sulfate brings little value to the product. Therefore, there is little markup in value in going from ammonia to ammonium sulfate, probably only enough to offset the cost crystallization, filtration and drying. This means that the soda ash must bear all of the costs for sodium sulfate, carbon dioxide, and most of the thermal energy and electricity costs.

The synthetic soda ash process based on sodium sulfate will use about 5.5 million BTUs of thermal heat as 450 psig steam per ton of product. At the current natural gas price of about \$6 per million BTU and a boiler operating at 85% efficiency, the cost of thermal energy will be about \$38.80 per ton. The soda ash plant will use about 0.138 MW-hr of electricity to produce one ton of soda ash. At \$45 per MW-hr, electricity will cost \$6.20 per ton of soda ash. Therefore, total energy cost for the soda ash will be about \$45 per ton. Labor and maintenance costs will be between \$20 and \$30 per ton of soda ash. This raises the cost of the soda ash to \$65 to \$75 per ton, excluding the costs of carbon dioxide and capital return.

The synthetic soda ash process based on sodium sulfate will consume about 0.5 tons of carbon dioxide to make a ton of soda ash. At the present price of about \$120 per ton, the carbon dioxide alone would cost \$60 per ton of soda ash. But from the discussion above, the carbon dioxide would have to be almost free for this process to have any economic chance of success.

The capital cost for a plant to produce 1.0 million tons per year of soda ash, consuming 1.35 million tons per year of sodium sulfate, will be about \$400 million. Capital recovery, assuming a 15 year recovery period, will add \$26.67 to the cost of the soda ash. I think from all of the above figures it is clear that the synthetic soda ash process based on sodium sulfate will not be economic.

### **3.3.3 React with KCl to Make K<sub>2</sub>SO<sub>4</sub>**

Potassium sulfate (K<sub>2</sub>SO<sub>4</sub>) is a higher value source of potassium for agriculture than potassium chloride (KCl). It is technically feasible to react sodium sulfate with KCl to produce K<sub>2</sub>SO<sub>4</sub> and NaCl. A process similar to this was operated in Searles Valley for many years, although not exactly the same process that would be required in a stand-alone plant.

This process consists of two parts. The first is a multistage, countercurrent leach section where sulfate solids feed the brine discharge stage, and KCl and water enter at the K<sub>2</sub>SO<sub>4</sub> product-crystallization stage. The second is a double-effect steam evaporator where the water in the discharge brine is evaporated to recover potassium and sulfate as solids for return to the leach process and crystalline sodium chloride for sale or disposal.

All  $K_2SO_4$  in the world market is produced from mineral deposits that contains both potassium and sulfate and is the primary product of the mineral extraction plant. Although some of the plants supplement their potassium resource with purchased KCl, in none of these operations is purchased KCl the primary potassium source. In contrast, all of the KCl for a plant based on agricultural drainage water would have to be purchased and transported to the plant site, and this would put that plant at a considerable financial disadvantage.

The plant in Utah uses a different brine chemistry to produce its  $K_2SO_4$ ; it uses a chemistry based on the K-Mg- $SO_4$ -Cl brine system instead of K-Na- $SO_4$ -Cl brine system. This allows the use of solar evaporation of the process discharge brine to reject the byproduct magnesium chloride and recover the potassium and sulfate. Since solar evaporation has a considerably lower cost than steam evaporation, it will give the Utah plant a further cost advantage versus a plant fed with pure sodium sulfate and KCl.

It is likely that even if this process had favorable economics, it would never become a major outlet for sodium sulfate. This is because the  $K_2SO_4$  market is relatively small. Total domestic production, almost all of it in Utah, is about 500,000 tons per year. I don't believe that all of this is sold domestically; part of it is sold to export markets where it competes primarily with product from Germany and Italy. Even if all of the current domestic production could be displaced, it would only consume 408,000 tons of sodium sulfate.

Finally, considerable process development would be required to build a plant to employ this process. While this would not be complicated, it would take a year or more to complete. It is beyond the scope of the current project to design a leach-evaporator-crystallizer plant to recover sodium chloride and potassium sulfate from sodium sulfate and potassium chloride.

#### **4.0     Onsite Storage of Mixed Agricultural Salts**

The data from the pilot test at Red Rock Ranch clearly demonstrate that accumulated salt can be leached from soil and that future buildup of salt in the soil can be prevented. Furthermore, there is a vast acreage in the San Joaquin Valley that would benefit from active control of salt buildup in the soil.

The renewable, long-term production of mixed agricultural salts appears to be about 827 tons per year for a one square-mile (640 acre) farm (communication from Vashek Chervinka). Even if an economic process can be developed to separate the mixed salts into salable products, one farm by itself will not produce enough mixed salt tonnage to warrant the high capital cost necessary to process the mixed salts into salable materials. It will be necessary have at least 1 million tons per year of mixed salts to support an economic-size salt separation operation. To provide at least 1 million tons per year of mixed salts, it will be necessary to collect the output from as much as 1,200 square miles of farmland.

It will take at least 10 years to build a production facility that can separate agricultural salts into salable commodities. This 10-year estimate is based on two years of research and bench-scale testing to confirm all technical aspects of the separation processes, one-and-a-half years for preliminary engineering to establish capital and operating costs and secure development capital, one year to design and construct a semi-works plant, two years of operation of the semi-works plant to demonstrate the process and develop all of the detailed design data needed for large-scale plant design. After that it will take a year for final plant design and two-and-a-half years for plant construction.

While a large plant is being constructed, it will be necessary to store the mixed salts produced from the surrounding farmland reclamation for ten years. This would require providing storage for about 10,000 tons of mixed salts per square mile of reclaimed land. If this can be stored at a density of 62 pounds per cubic foot, about 325,000 cubic feet (one acre-foot) of salt would have to be stored. If this could be stored in a pile 20 feet deep, the area that would have to be dedicated to salt storage would be just (16,250 ft<sup>2</sup> or about 130 feet square). This is about 0.06% of the land in a one square-mile farm.

The salt storage pile must be built with a double, impermeable liner with geo-netting leak detection across the bottom and up the walls to the top to protect the groundwater beneath the pond. Also, if the storage pile were built like this, it would also be possible to use the surface of the pile to evaporate the saturated brine, leaving the pre-concentration solar evaporation pond(s) to dryness. If the mixed salts could be deposited directly on the storage pile in this manner, the cost for salt harvesting could be delayed until the salt is removed for feed for the processing plant. As such, it is the lowest-cost option for handling the salt during the interim period.

## **APPENDIX A – Analysis of Red Rock Data**

Page A-1	Red Rock Ranch Data, Expanded and Interpreted
Page A-2	Red Rock Ranch Data, Expanded and Interpreted
Page A-3	Red Rock Ranch Data, Expanded and Interpreted
Page A-4	Red Rock Ranch Data, Expanded and Interpreted
Page A-5	Figure of Concentration Ratios
Page A-6	Figure and Correlation for Conductance Measurements
Page A-7	Figure of Concentration Ratios, 29 July 2003
Page A-8	Figure of Concentration Ratios, 29 November 2003
Page A-9	Figure of Concentration Ratios, 28 January 2004
Page A-10	Figure of Concentration Ratios, 29 March 2004
Page A-11	Figure of Concentration Ratios, 31 August 2004
Page A-12	Expected Solar Radiation at Red Rock Ranch

# Red Rock Ranch Pilot Plant Raw and Reduced Analytical Data - Page 1

Collection Date	25-Jun-03	29-Jul-03	29-Jul-03	29-Jul-03	29-Jul-03	25-Aug-03	25-Aug-03	25-Aug-03	25-Aug-03	25-Aug-03	24-Sep-03	24-Sep-03	24-Sep-03	24-Sep-03	24-Sep-03	24-Sep-03	31-Aug-04	31-Aug-04	31-Aug-04	31-Aug-04	31-Aug-04	31-Aug-04
Station	Sump D	Sump D	TT1	TT3	S.E.D	Sump D	TT1	TT3	S.E.D	TT2	Sump D	S.E.D	TT3	TT4	RRR-S.B.	Sump D	TT2	TT3	TT4	Sit Crystal	TT-3	S.E.D
Conductance (EC) uS/cm	14,270	13,590	54,820	117,300	63,390	13,750	43,540	136,400	23,170	84,500	11,660	26,750	121,800	65,970	163,000	16,300	98,640	177,600	151,400	72,110		38,600
Dissolved Bicarbonate (HCO3-) (as CaCO3)	332	300	380	744	397	252	271	961	259	526		252	289	796	399		180	550	2,051	986	110	276
Dissolved Boron (mg/L)	23										17	20					20	215	1,160	479	49.3	59.8
Dissolved Calcium (mg/L)	605	579	686	563	678	606	678	578	700	570	588	679	605	585	673		587	593	200	524	100	441
Dissolved Carbonate (CO3=) (as CaCO3)	1	1	2	5	3	1	3	10	2	7		1	1	3	3		1	9	7	13	4	4
Dissolved Chloride (mg/L)	2,700	2,740	16,300	46,000	18,700	2,770	11,000	57,500	5,020	26,300	1,960	2,940	5,340	46,300	17,900	141,000	3,130	29,500	152,000	63,500	32,000	8,890
Dissolved Magnesium (mg/L)	192	191	1,010	3,080	1,200	190	758	4,470	340	1,730	163	207	416	3,360	1,400	9,090	192	2,020	11,600	4,120	517	517
Dissolved Nitrate (mg/L)	422					482	1,750	8,320	805	3,970	389	523	1,000	7,500	3,220		644	5,010	25,200	10,100	1,080	1,450
Dissolved Potassium (mg/L)	4.8	5.6	37	105	42	6	23	144	11	61	10	10	25	95	35.4		5.3	68.3	308	122	50	25
Dissolved Selenium (mg/L)	0.905	0.975	5.35	14.4	6.15	0.975	3.4	14.8	1.43	7.5	0.72	1.18	2.2	14.9	7.05	35.7	1.63	11.4	41.4	21	2.02	3.53
Dissolved Silica (SiO2) mg/L	31.2	33				32						31					31.2					
Dissolved Sodium (mg/L)	2,890	2,620	15,800	46,500	21,200	2,530	10,300	62,700	5,310	25,700	2,340	2,800	6,230	46,700	20,300	133,000	2,730	35,200	115,000	64,700	20,400	8,980
Dissolved Sulfate (mg/L)	4,020	4,000	15,800	47,000	19,000	3,690	11,700	59,700	6,200	27,400	3,830	3,920	8,730	49,500	21,200	125,000	3,740	34,100	88,800	66,200	3,750	10,600
Dissolved Hardness (as CaCO3)	2,302	2,233	5,873	14,100	6,636	2,296	4,815	19,854	3,149	8,549	2,140	2,548	3,224	15,300	7,447		2,257	9,800	49,161	18,277	2,142	3,231
pH	7.1	6.9	7.7	7.8	7.8	7.3	8	8	7.9	8.1	7.1	7	7.7	7.5	7.8		7.2	8.2	7.5	8.1		8.2
Total Alkalinity (mg/L) (as CaCO3)	332	300	382	748	399	252	274	970	261	532	282	252	290	798	401		180	558	2,057	998		280
Total Dissolved Solids (mg/L)	9,440	8,850	35,560	77,100	42,100	8,920	28,180	89,800	15,040	55,800	9,256	10,890	22,100	152,100	63,700	206,400	11,110	103,700	402,000	213,700	55,600	32,760

## Concentration ratios

Boron Conc Ratio	1.000											1.000					1	10.75	58	23.95	2.465	2.99
Chloride Conc Ratio	1.000	1.015	6.037	17.037	6.926	1.000	3.971	20.758	1.812	9.495		1.000	1.816	15.748	6.088		1	9.425	48.562	20.288	10.224	2.840
Magnesium Conc Ratio	1.000	0.995	5.260	16.042	6.250	1.000	3.989	23.526	1.789	9.105		1.000	2.010	16.232	6.763		1	10.521	60.417	21.458	2.693	2.693
Nitrate Conc Ratio	1.000					1.000	3.631	17.261	1.670	8.237		1.000	1.912	14.340	6.157		1	7.780	39.130	15.683	1.677	2.252
Potassium Conc Ratio	1.000	1.167	7.708	21.875	8.750	1.000	3.833	24.000	1.833	10.167		1.000	2.500	9.500	3.540		1	12.887	58.113	23.019	9.434	4.717
Selenium Conc Ratio	1.000	1.077	5.912	15.912	6.796	1.000	3.487	15.179	1.467	7.692		1.000	1.864	12.627	5.975		1	6.994	25.399	12.883	1.239	2.166
Sodium Conc Ratio	1.000	0.907	5.467	16.090	7.336	1.000	4.071	24.783	2.099	10.158		1.000	2.225	16.679	7.250		1	12.894	42.125	23.700	7.473	3.289
Sulfate Conc Ratio	1.000	0.995	3.930	11.692	4.726	1.000	3.171	16.179	1.680	7.425		1.000	2.227	12.628	5.408		1	9.118	23.743	17.701	1.003	2.834
Sulfate Conc Ratio, Ca & HCO3 corrected	1.000	1.010	5.254	16.858	6.436	1.000	4.327	24.922	1.970	11.146		1.000	3.074	20.088	8.195		1	13.616	36.912	27.039	1.473	3.999
Bicarbonate Conc Ratio	1.000	0.904	1.145	2.241	1.196	1.000	1.075	3.813	1.028	2.087		1.000	1.147	3.159	1.583		1	3.056	11.394	5.478	0.611	1.533
Calcium Conc Ratio	1.000	0.957	1.134	0.931	1.121	1.000	1.119	0.954	1.155	0.941		1.000	0.891	0.862	0.991		1	1.010	0.341	0.893	0.170	0.751

## Molarities, millimoles/liter

Bicarbonate (HCO3-), mmol/L	3.32	3.00	3.80	7.43	3.97	2.52	2.71	9.60	2.59	5.26	0.00	2.52	2.89	7.95	3.99		1.80	5.50	20.49	9.85	1.10	2.76
Boron, mmol/L	2.13											1.57	1.85					1.85	19.89	107.31	44.31	4.56
Calcium, mmol/L	15.09	14.45	17.12	14.05	16.92	15.12	16.92	14.42	17.47	14.22	14.67	16.94	15.09	14.60	16.79			14.65	14.80	4.99	13.07	2.50
Carbonate (CO3=), mmol/L	0.010	0.010	0.020	0.050	0.030	0.010	0.030	0.100	0.020	0.070		0.010	0.010	0.030	0.030			0.010	0.090	0.070	0.130	0.040
Chloride, mmol/L	76.16	77.29	459.80	1,297.60	527.50	78.14	310.30	1,622.00	141.61	741.89	55.29	82.93	150.63	1,306.06	504.94	3,977.43	88.29	832.16	4,287.73	1,791.26	902.68	250.78
Magnesium, mmol/L	7.90	7.86	41.55	126.70	49.36	7.82	31.18	183.87	13.99	71.16	6.71	8.52	17.11	138.21	57.59	373.92	7.90	83.09	477.17	169.48	21.27	21.27
Nitrate, mmol/L	6.81					7.77	28.22	134.17	12.98	64.02	6.27	8.43	16.13	120.95	51.93		10.39	80.79	406.39	162.88	17.42	23.38
Potassium, mmol/L	0.123	0.143	0.946	2.685	1.074	0.153	0.588	3.683	0.281	1.560	0.256	0.256	0.639	2.430	0.905		0.136	1.747	7.877	3.120	1.279	0.639
Selenium, mmol/L	0.011	0.012	0.068	0.182	0.078	0.012	0.043	0.187	0.018	0.095	0.009	0.015	0.028	0.189	0.089	0.45	0.021	0.144	0.524	0.266	0.026	0.045
Silica, mmol/L	0.519	0.549				0.533						0.516					0.519					
Sodium, mmol/L	90.12	81.70	492.67	1,449.95	661.05	78.89	321.17	1,955.10	165.58	801.37	72.97	87.31	194.26	1,456.19	632.99	4,147.18	85.13	1,097.60	3,585.91	2,017.46	636.11	280.01
Sulfate, mmol/L	41.84	41.64	164.46	489.23	197.77	38.41	121.79	621.42	64.54	285.21	39.87	40.80	90.87	515.25	220.67	1,301.13	38.93	354.95	924.33	689.08	39.03	110.34
Ca/SO4 mole ratio	0.36	0.35	0.10	0.03	0.09	0.39	0.14	0.02	0.27	0.05	0.37	0.42	0.17	0.03	0.08		0.38	0.04	0.01	0.02	0.06	0.10
Ionic Strength, mmol/L	258.6	240.5	1,197.5	3,401.9	1,474.6	243.9	849.8	4,558.9	436.5	1,999.0	212.3	266.5	502.8	3,576.4	1,506.7		263.7	2,505.5	9,827.8	4,914.0	1,628.5	716.8

## Weight Percents

Estimated Sp Grav	1.008	1.008	1.031	1.067	1.037	1.008	1.025	1.079	1.013	1.049	1.008	1.010	1.019	1.133	1.056	1.181	1.010	1.091	1.352	1.187	1.049	1.029
Water (H2O), grams/L	998.8	998.9	995.6	990.4	994.7	998.9	996.5	988.8	998.1	993.0	998.8	998.6	997.2	981.0	992.0	974.2	998.6	987.0	949.8	973.3	993.1	995.9
Weight of liter of water, grams	1,008.3	1,007.7	1,031.1	1,067.5	1,036.8	1,007.8	1,024.7	1,078.6	1,013.2	1,048.8	1,008.1	1,009.5	1,019.3	1,133.1	1,055.7	1,180.6	1,009.7	1,090.7	1,351.8	1,187.0	1,048.7	1,028.7
Water (H2O), wt %	99.06%	99.12%	96.55%	92.78%	95.94%	99.11%	97.25%	91.67%	98.52%	94.68%	99.08%	98.92%	97.83%	86.58%	93.97%	82.52%	98.90%	90.49%	70.26%	82.00%	94.70%	96.82%
Bicarbonate (HCO3-), wt %	0.0201%	0.0181%	0.0225%	0.0425%	0.0233%	0.0152%	0.0161%	0.0543%	0.0156%	0.0306%	0.0000%	0.0152%	0.0173%	0.0428%	0.0230%		0.0109%	0.0307%	0.0925%	0.0506%	0.0064%	0.0164%
Boron as boric acid, wt %	0.0130%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0096%	0.0113%	0.0000%	0.0000%	0.0000%	0.0000%	0.0113%	0.1128%	0.4909%	0.2308%	0.0269%	0.0333%
Calcium, wt %	0.0600%	0.0575%	0.0665%	0.0527%	0.0654%	0.0601%	0.0662%	0.0536%	0.0691%	0.0543%	0.0583%	0.0673%	0.0594%	0.0516%	0.0637%	0.0000%	0.0581%	0.0544%	0.0148%	0.0441%	0.0095%	0.0429%
Carbonate (CO3=), wt %	0.0001%	0.0001%	0.0001%	0.0003%	0.0002%	0.0001%	0.0002%	0.0006%	0.0001%	0.0004%	0.0000%	0.0001%	0.0001%	0.0002%	0.0002%		0.0001%	0.0005%	0.0003%	0.0007%	0.0002%	0.0002%
Chloride, wt %	0.27%	0.27%	1.58%	4.31%	1.80%	0.27%	1.07%	5.33%	0.50%	2.51%	0.19%	0.29%	0.52%	4.09%	1.70%	11.94%	0.31%	2.70%	11.24%	5.35%	3.05%	0.86%
Magnesium, wt %	0.0190%	0.0190%	0.0980%	0.2885%	0.1157%	0.0189%	0.0740%	0.4144%	0.0336%	0.1649%	0.0162%	0.0205%	0.0408%	0.2965%	0.1326%	0.7699%	0.0190%	0.1852%	0.8581%	0.3471%	0.0493%	0.0503%
Nitrate, wt %	0.0419%	0.0000%	0.0000%	0.0000%	0.0000%	0.0478%	0.1708%	0.7714%	0.0795%	0.3785%	0.0386%	0.0518%	0.0981%	0.6619%	0.3050%	0.0000%	0.0638%	0.4593%	1.8643%	0.8509%	0.1030%	0.1410%
Potassium, wt %	0.0005%	0.0006%	0.0036%	0.0098%	0.0041%	0.0006%	0.0022%	0.0134%	0.0011%	0.0058%	0.0010%	0.0010%	0.0025%	0.0084%	0.0034%		0.0005%	0.0063%	0.0228%	0.0103%	0.0048%	0.0024%
Selenium, wt %	0.0001%	0.0001%	0.0005%	0.0013%	0.0006%	0.0001%	0.0003%	0.0014%	0.0001%	0.0007%	0.0001%	0.0001%	0.0002%	0.0013%	0.0007%	0.0030%	0.0002%	0.0010%	0.0031%	0.0018%	0.0002%	0.0003%
Silica, wt %	0.0031%	0.0033%	0.0000%	0.0000%	0.0000%	0.0032%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0031%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0031%	0.0000%	0.0000%	0.0000%	0.0000%
Sodium, wt %	0.29%	0.26%	1.53%	4.36%	2.04%	0.25%	1.01%	5.81%	0.52%	2.45%	0.23%	0.28%	0.61%	4.12%	1.92%	11.27%	0.27%	3.23%	8.51%	5.45%	1.95%	0.87%
Sulfate, wt %	0.40%	0.40%	1.53%	4.36%	1.83%	0.37%	1.14%	5.54%	0.61%	2.61%	0.38%	0.39%	0.86%	4.37%	2.01%	10.59%	0.77%	3.13%	6.57%	5.58%	1.36%	1.03%

# Red Rock Ranch Pilot Plant Raw and Reduced Analytical Data - Page 2

Collection Date	27-Jul-04	27-Jul-04	27-Jul-04	27-Jul-04	27-Jul-04	29-Jun-04	29-Jun-04	29-Jun-04	29-Jun-04	29-Jun-04	29-Jun-04	24-May-04	24-May-04	24-May-04	24-May-04	24-May-04	29-Mar-04	29-Mar-04	29-Mar-04	29-Mar-04	29-Mar-04	29-Mar-04	29-Mar-04			
Station	Sump D	TT2	TT3	Slt Crystal	S.E.D	Sump C	Sump D	TT3	TT4	Slt Crystal	TT-3	S.E.D	Sump D	TT3	TT4	Slt Crystal	TT-3	S.E.D	Sump C	Sump D	TT1	TT2	TT3	Slt Crystal	TT-3	S.E.D
Conductance (EC) uS/cm	14,750	101,400	172,400	98,630	109,100	12,420	14,620	166,000	166,400	90,550	89,410	18,060	175,400	152,400	58,410	67,660	11,860	14,700	46,410	77,040	149,200	38,370	26,470			
Dissolved Bicarbonate (HCO3-) (as CaCO3)	237	579	2,018	82	663		320	2,619	1,406	96	490	356	1,468	1,066	119	446	20	338	353	506	1,158	26	314			
Dissolved Boron (mg/L)	20	237	1,160	33	252	18.8	21.3	1,580	805	42	206	22	1,410	487	36.2	125	16.9	21.2	88	188	572	4.4	46			
Dissolved Calcium (mg/L)	668	1,000	1,000	100	1,000	568	620	200	346	100	705	604	100	533	446	629	641	671	750	758	679	109	679			
Dissolved Carbonate (CO3=) (as CaCO3)	1	4	26	1	5		1	1	36	1	2	3	6	9	8	7	20	1	15	13	15	1	4			
Dissolved Chloride (mg/L)	2,980	34,300	138,000	42,300	37,100	2,220	2,930	155,000	106,000	37,600	28,700	3,480	151,000	69,400	4,710	18,900	2,210	2,980	12,000	23,200	73,600	528	5,990			
Dissolved Magnesium (mg/L)	209	2,220	12,500	488	2,590	162	201	15,500	7,400	439	1,990	246	11,700	5,500	320	1,190	164	259	848	1,710	6,290	40	441			
Dissolved Nitrate (mg/L)	524	4,600	26,800	803	4,570	292	388	36,900	12,500	953	3,330	409	25,900	9,500	796	2,220	271	353	1,550	3,030	11,200	106	723			
Dissolved Potassium (mg/L)	100	500	500	50	500	10	10	405	192	50	58	10	344	150	13.3	33	5	5	25	40	155	5	11.2			
Dissolved Selenium (mg/L)	1.41	11.1	42.5	1.77	11.1	0.671	0.965	53.6	27.3	2.07	7.77	1.12	40.9	19.2	6.7	3.45	0.67	0.883	3.95	7.79	23.1	4.57	1.88			
Dissolved Silica (SiO2) mg/L	38.1						31.7					34					20	35.1								
Dissolved Sodium (mg/L)	2,780	33,400	116,000	24,700	41,100	2,450	2,940	131,000	12,100	25,000	31,000	3,780	126,000	75,800	21,700	20,100	2,260	2,910	12,500	24,200	81,500	13,300	6,730			
Dissolved Sulfate (mg/L)	3,700	34,700	88,200	6,050	41,700	3,880	4,190	93,300	107,000	7,390	29,900	5,230	92,000	66,800	39,800	20,500	3,490	4,180	13,700	25,900	61,300	27,300	7,460			
Dissolved Hardness (as CaCO3)	2,529	11,059	52,314	2,010	12,508	2,086	2,376	63,998	31,342	1,905	9,957	2,522	48,360	23,984	2,432	6,472	2,276	2,743	5,366	8,936	27,602	437	3,511			
pH	7.2	7.8	8.1		7.9	7.3	7.2	6.7	8.4		7.7	7.9	7.6	7.9	8.8	8.2	7.7	7.6	8.6	8.4	8.1	8.4	8.1			
Total Alkalinity (mg/L) (as CaCO3)	237	582	2,042	83	668	310	320	2,620	1,439	97	492	359	1,474	1,074	126	453	353	339	366	518	1,172	27	318			
Total Dissolved Solids (mg/L)	11,130	106,900	373,000	73,800	123,400	9,730	11,100	415,000	327,100	69,400	91,000	14,480	316,500	220,300	65,780	63,200	9,180	11,390	40,920	75,000	211,400	40,120	21,100			

## Concentraton ratios

Boron Conc Ratio	1.000	11.850	58.000	1.650	12.600		1.000	74.178	37.793	1.972	9.671	1.000	64.091	22.136	1.645	5.682		1.000	4.151	8.868	26.981	0.208	2.170
Chloride Conc Ratio	1.000	11.510	46.309	14.195	12.450		1.000	52.901	36.177	12.833	9.795	1.000	43.391	19.943	1.353	5.431		1.000	4.027	7.785	24.698	0.177	2.010
Magnesium Conc Ratio	1.000	10.622	59.809	2.335	12.392		1.000	77.114	38.616	2.184	9.900	1.000	47.561	22.358	1.301	4.837		1.000	3.274	6.602	24.286	0.154	1.703
Nitrate Conc Ratio	1.000	8.779	51.145	1.532	8.721		1.000	95.103	32.216	2.456	8.582	1.000	63.325	23.227	1.946	5.428		1.000	4.391	8.584	31.728	0.300	2.048
Potassium Conc Ratio	1.000	5.000	5.000	0.500	5.000		1.000	40.500	19.200	5.000	5.800	1.000	34.400	15.000	1.330	3.300		1.000	5.000	8.000	31.000	1.000	2.240
Selenium Conc Ratio	1.000	7.872	30.142	1.255	7.872		1.000	55.544	28.290	2.145	8.052	1.000	36.518	17.143	5.982	3.080		1.000	4.473	8.822	26.161	5.176	2.129
Sodium Conc Ratio	1.000	12.014	41.727	8.885	14.784		1.000	44.558	4.116	8.503	10.544	1.000	33.333	20.053	5.741	5.317		1.000	4.296	8.316	28.007	4.570	2.313
Sulfate Conc Ratio	1.000	9.378	23.838	1.635	11.270		1.000	22.267	25.537	1.764	7.136	1.000	17.591	12.772	7.610	3.920		1.000	3.278	6.196	14.665	6.531	1.785
Sulfate Conc Ratio, Ca & HCO3 corrected	1.000	14.725	39.217	2.644	17.907		1.000	32.923	37.392	2.518	9.955	1.000	23.391	16.704	9.812	4.859		1.000	4.416	8.898	22.031	9.895	2.189
Bicarbonate Conc Ratio	1.000	2.443	8.515	0.346	2.797		1.000	8.184	4.394	0.300	1.531	1.000	4.124	2.994	0.334	1.253		1.000	1.044	1.497	3.426	0.077	0.929
Calcium Conc Ratio	1.000	1.497	1.497	0.150	1.497		1.000	0.323	0.558	0.161	1.137	1.000	0.166	0.882	0.738	1.041		1.000	1.118	1.130	1.012	0.162	1.012

## Molarities, millimoles/liter

Bicarbonate (HCO3-), mmol/L	2.37	5.78	20.16	0.82	6.62		3.20	26.17	14.05	0.96	4.90	3.56	14.67	10.65	1.19	4.46	0.20	3.38	3.53	5.06	11.57	0.26	3.14
Boron, mmol/L	1.85	21.92	107.31	3.05	23.31	1.74	1.97	146.16	74.47	3.89	19.06	2.04	130.43	45.05	3.35	11.56	1.56	1.96	8.14	17.39	52.91	0.41	4.26
Calcium, mmol/L	16.67	24.95	24.95	2.50	24.95	14.17	15.47	4.99	8.63	2.50	17.59	15.07	2.50	13.30	11.13	15.69	15.99	16.74	18.71	18.91	16.94	2.72	16.94
Carbonate (CO3=), mmol/L	0.010	0.040	0.260	0.010	0.050		0.010	0.010	0.360	0.010	0.020	0.030	0.060	0.090	0.080	0.070	0.200	0.010	0.150	0.130	0.150	0.010	0.040
Chloride, mmol/L	84.06	967.56	3,892.81	1,193.23	1,046.54	62.62	82.65	4,372.36	2,990.13	1,060.65	809.59	98.17	4,259.52	1,957.69	132.86	533.15	62.34	84.06	338.50	654.44	2,076.16	14.89	168.97
Magnesium, mmol/L	8.60	91.32	514.19	20.07	106.54	6.66	8.27	637.60	304.40	18.06	81.86	10.12	481.28	226.24	13.16	48.95	6.75	10.65	34.88	70.34	258.74	1.65	18.14
Nitrate, mmol/L	8.45	74.18	432.19	12.95	73.70	4.71	6.26	595.07	201.58	15.37	53.70	6.60	417.67	153.20	12.84	35.80	4.37	5.69	25.00	48.86	180.62	1.71	11.66
Potassium, mmol/L	2.558	12.788	12.788	1.279	12.788	0.256	0.256	10.358	4.910	1.279	1.483	0.256	8.798	3.836	0.340	0.844	0.128	0.128	0.639	1.023	3.964	0.128	0.286
Selenium, mmol/L	0.018	0.141	0.538	0.022	0.141	0.008	0.012	0.679	0.346	0.026	0.098	0.014	0.518	0.243	0.085	0.044	0.008	0.011	0.050	0.099	0.293	0.058	0.024
Silica, mmol/L	0.634						0.528					0.566					0.333	0.584					
Sodium, mmol/L	86.69	1,041.47	3,617.09	770.19	1,281.57	76.40	91.67	4,084.81	377.30	779.54	966.64	117.87	3,928.91	2,363.58	676.64	626.75	70.47	90.74	389.77	754.60	2,541.32	414.72	209.85
Sulfate, mmol/L	38.51	361.19	918.08	62.97	434.06	40.39	43.61	971.17	1,113.77	76.92	311.23	54.44	957.64	695.33	414.28	213.39	36.33	43.51	142.60	269.60	638.08	284.17	77.65
Ca/SO4 mole ratio	0.43	0.07	0.03	0.04	0.06	0.35	0.35	0.01	0.01	0.03	0.06	0.28	0.00	0.02	0.03	0.07	0.44	0.38	0.13	0.07	0.03	0.01	0.22
Ionic Strength, mmol/L	266.4	2,626.3	9,565.3	2,069.6	3,035.2	221.1	268.8	10,854.4	5,098.6	1,961.7	2,283.8	323.2	10,204.5	5,482.5	1,277.1	1,506.4	214.3	273.6	980.7	1,859.4	5,797.7	723.4	527.9

## Weight Percents

Estimated Sp Grav	1.010	1.094	1.326	1.065	1.108	1.009	1.010	1.363	1.286	1.061	1.080	1.013	1.277	1.193	1.058	1.055	1.008	1.010	1.036	1.066	1.185	1.035	1.018
Water (H2O), grams/L	998.6	986.6	953.4	990.8	984.6	998.6	998.6	948.1	959.1	991.3	988.6	998.2	960.4	972.5	991.8	992.1	998.9	998.6	994.9	990.6	973.6	995.0	997.4
Weight of liter of water, grams	1,009.7	1,093.5	1,326.4	1,064.6	1,108.0	1,008.5	1,009.7	1,363.1	1,286.2	1,060.7	1,079.6	1,012.7	1,276.9	1,192.8	1,057.6	1,055.3	1,008.0	1,010.0	1,035.8	1,065.6	1,185.0	1,035.1	1,018.5
Water (H2O), wt %	98.90%	90.22%	71.88%	93.07%	88.86%	99.04%	98.90%	69.56%	74.57%	93.46%	91.57%	98.57%	75.21%	81.53%	93.78%	94.01%	99.09%	98.87%	96.05%	92.96%	82.16%	96.12%	97.93%
Bicarbonate (HCO3-), wt %	0.0143%	0.0323%	0.0928%	0.0047%	0.0365%	0.0000%	0.0193%	0.1171%	0.0666%	0.0055%	0.0277%	0.0214%	0.0701%	0.0545%	0.0069%	0.0258%	0.0012%	0.0204%	0.0208%	0.0289%	0.0596%	0.0015%	0.0188%
Boron as boric acid, wt %	0.0113%	0.1240%	0.5003%	0.0177%	0.1301%	0.0107%	0.0121%	0.6630%	0.3580%	0.0226%	0.1091%	0.0124%	0.6316%	0.2335%	0.0196%	0.0678%	0.0096%	0.0120%	0.0486%	0.1009%	0.2761%	0.0024%	0.0258%
Calcium, wt %	0.0662%	0.0914%	0.0754%	0.0094%	0.0903%	0.0563%	0.0614%	0.0147%	0.0269%	0.0094%	0.0653%	0.0596%	0.0078%	0.0447%	0.0422%	0.0596%	0.0636%	0.0664%	0.0724%	0.0711%	0.0573%	0.0105%	0.0627%
Carbonate (CO3=), wt %	0.0001%	0.0002%	0.0012%	0.0001%	0.0003%	0.0000%	0.0001%	0.0000%	0.0017%	0.0001%	0.0001%	0.0002%	0.0003%	0.0005%	0.0005%	0.0004%	0.0012%	0.0001%	0.0009%	0.0007%	0.0008%	0.0001%	0.0002%
Chloride, wt %	0.30%	3.14%	10.40%	3.97%	3.35%	0.22%	0.29%	11.37%	8.04%	3.54%	2.66%	0.34%	11.83%	5.82%	0.45%	1.79%	0.22%	0.30%	1.16%	2.18%	6.21%	0.05%	0.59%
Magnesium, wt %	0.0207%	0.2030%	0.9424%	0.0458%	0.2338%	0.0161%	0.0199%	1.1371%	0.5753%	0.0414%	0.1843%	0.0243%	0.9163%	0.4611%	0.0303%	0.1128%	0.0163%	0.0256%	0.0819%	0.1605%	0.5308%	0.0039%	0.0433%
Nitrate, wt %	0.0519%	0.4207%	2.0205%	0.0754%	0.4125%	0.0290%	0.0384%	2.7070%	0.9718%	0.0898%	0.3084%	0.0404%	2.0283%	0.7965%	0.0753%	0.2104%	0.0269%	0.0350%	0.1496%	0.2843%	0.9452%	0.0102%	0.0710%
Potassium, wt %	0.0099%	0.0457%	0.0377%	0.0047%	0.0451%	0.0010%	0.0010%	0.0297%	0.0149%	0.0047%	0.0054%	0.0010%	0.0269%	0.0126%	0.0013%	0.0031%	0.0005%	0.0005%	0.0024%	0.0038%	0.0131%	0.0005%	0.0011%
Selenium, wt %	0.0001%	0.0010%	0.0032%	0.0002%	0.0010%	0.0001%	0.0001%	0.0039%	0.0021%	0.0002%	0.0007%	0.0001%	0.0032%	0.0016%	0.0006%	0.0003%	0.0001%	0.0001%	0.0004%	0.0007%	0.0019%	0.0004%	0.0002%
Silica, wt %	0.0038%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0031%	0.0000%	0.0000%	0.0000%	0.0000%	0.0034%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0020%	0.0035%	0.0000%	0.0000%	0.0000%	0.0000%
Sodium, wt %	0.28%	3.05%	8.75%	0.52%	3.71%	0.24%	0.29%	9.61%	0.94%	2.36%	2.87%	0.37%	9.87%	6.35%	2.05%	1.90%	0.22%	0.29%	1.21%	2.27%	6.88%	1.28%	0.66%
Sulfate, wt %	0.37%	3.17%	6.65%	0.37%	3.76%	0.38%	0.41%	6.84%	8.32%	0.70%	2.77%	0.52%	7.20%	5.60%	3.76%	1.94%	0.35%	0.41%	1.32%	2.43%	5.17%	2.64%	0.73%

# Red Rock Ranch Pilot Plant Raw and Reduced Analytical Data - Page 3

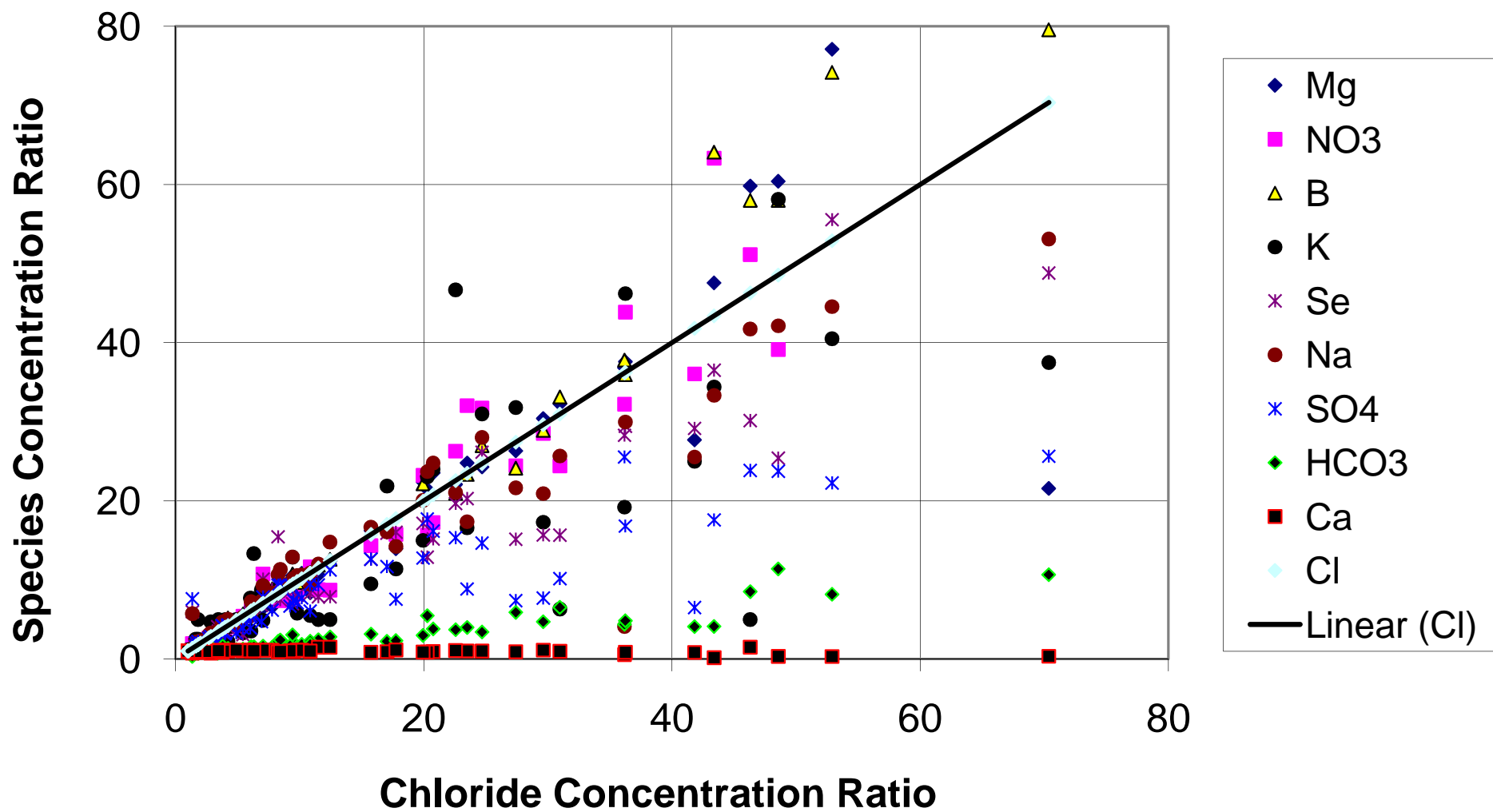
Collection Date	26-Apr-04	26-Apr-04	26-Apr-04	26-Apr-04	11-Mar-04	11-Mar-04	11-Mar-04	11-Mar-04	28-Jan-04	28-Jan-04	28-Jan-04	28-Jan-04	28-Jan-04	22-Dec-03	22-Dec-03	22-Dec-03	22-Dec-03	22-Dec-03	22-Dec-03
Station	Sump D	TT3	TT4	S.E.D	Sump D	TT3	TT4	S.E.D	Sump D	TT2	TT3	TT4	S.E.D	Sump C	Sump D	TT2	TT3	TT4	S.E.D
Conductance (EC) uS/cm	15,290	171,600	99,550	89,090	15,840	115,000	70,000	45,670	13,870	44,980	165,000	94,100	23,330	13,720	14,020	47,630	164,000	89,200	24,470
Dissolved Bicarbonate (HCO3-) (as CaCO3)	325	1,575	602	547	334	1,333	546	249	221	327	1304	495	160		216	351	1412	520	251
Dissolved Boron (mg/L)	21	755	224	198	24	560	205	93	24	95	579	234	45	23	19.1	92	633	193	44
Dissolved Calcium (mg/L)	632	534	705	665	620	640	683	688	681	571	629	629	648	548	607	577	598	582	514
Dissolved Carbonate (CO3=) (as CaCO3)	2	10	8	7	1	13	11	4	1	13	13	13	2		1	7	9	8	3
Dissolved Chloride (mg/L)	3,090	112,000	31,400	28,500	3,320	78,000	23,400	11,300	2,940	11,000	80,600	24,300	5,330	2,340	2,890	11,000	89,500	24,400	4,760
Dissolved Magnesium (mg/L)	217	8,160	2,350	1,970	230	5,700	2,140	810	212	811	5,580	1,910	387	167	181	786	5,840	1,720	344
Dissolved Nitrate (mg/L)	399	17,500	4,080	3,540	362	11,600	3,890	1,550	536	1,890	13,100	4,150	852	420	565	1,970	13,800	4,170	850
Dissolved Potassium (mg/L)	5	231	53	48	10	166	49	25	5	19	159	42	25	10	25	50	158	50	25
Dissolved Selenite (mg/L)	0.975	28.7	9.97	8.36	1.03	20.9	10.4	4.21	1.32	4.75	20	20.4	2.1	1.02	1.38	4.65	21.6	10.3	2.31
Dissolved Silica (SiO2) mg/L	31.4				29.3														
Dissolved Sodium (mg/L)	2,970	89,000	31,600	28,400	3,290	57,100	30,600	11,700	2,680	12,400	58,000	28,600	5,340	2,620	2,470	11,600	63,400	28,000	5,350
Dissolved Sulfate (mg/L)	4,260	71,600	32,900	28,500	4,280	37,900	33,600	12,200	3,590	15,100	26,500	33,500	6,090	4,420	3,540	14,800	36,000	33,200	7,150
Dissolved Hardness (as CaCO3)	2,472	34,936	11,437	9,775	2,609	25,071	10,520	5,633	2,574	4,770	24,550	9,436	3,212	2,056	2,261	4,678	25,546	8,538	2,701
pH	7.7	7.8	8.1	8.1	7.6	8	8.3	8.2	7.6	8.6	8	8.4	8.1	7.7	7.7	8.3	7.8	8.2	8.1
Total Alkalinity (mg/L) (as CaCO3)	327	1,584	609	554	335	1,346	556	253	222	339	1,316	507	162	307	217	358	1,420	528	254
Total Dissolved Solids (mg/L)	11,970	292,300	105,300	88,200	12,020	164,200	80,700	39,900	10,550	41,020	187,000	88,600	18,540	10,910	10,350	41,440	199,400	88,600	19,850
<b>Concentration ratios</b>																			
Boron Conc Ratio	1.000	35.952	10.667	9.429	1.000	23.333	8.542	3.875	1.000	3.958	24.125	9.750	1.875		1.000	4.817	33.141	10.105	2.304
Chloride Conc Ratio	1.000	36.246	10.162	9.223	1.000	23.484	7.048	3.404	1.000	3.741	27.415	8.265	1.813		1.000	3.806	30.969	8.443	1.647
Magnesium Conc Ratio	1.000	37.604	10.829	9.078	1.000	24.783	9.304	3.522	1.000	3.825	26.321	9.009	1.825		1.000	4.343	32.265	9.503	1.901
Nitrate Conc Ratio	1.000	43.860	10.226	8.872	1.000	32.044	10.746	4.282	1.000	3.526	24.440	7.743	1.590		1.000	3.487	24.425	7.381	1.504
Potassium Conc Ratio	1.000	46.200	10.600	9.600	1.000	16.600	4.900	2.500	1.000	3.800	31.800	8.400	5.000		1.000	2.000	6.320	2.000	1.000
Selenium Conc Ratio	1.000	29.436	10.226	8.574	1.000	20.291	10.097	4.087	1.000	3.598	15.152	15.455	1.591		1.000	3.370	15.652	7.464	1.674
Sodium Conc Ratio	1.000	29.966	10.640	9.562	1.000	17.356	9.301	3.556	1.000	4.627	21.642	10.672	1.993		1.000	4.696	25.668	11.336	2.166
Sulfate Conc Ratio	1.000	16.808	7.723	6.690	1.000	8.855	7.850	2.850	1.000	4.206	7.382	9.331	1.696		1.000	4.181	10.169	9.379	2.020
Sulfate Conc Ratio, Ca & HCO3 corrected	1.000	24.500	10.858	9.365	1.000	12.527	10.908	3.612	1.000	6.730	12.413	15.617	2.236		1.000	6.207	16.103	14.645	2.759
Bicarbonate Conc Ratio	1.000	4.846	1.852	1.683	1.000	3.991	1.635	0.746	1.000	1.480	5.900	2.240	0.724		1.000	1.625	6.537	2.407	1.162
Calcium Conc Ratio	1.000	0.845	1.116	1.052	1.000	1.032	1.102	1.110	1.000	0.838	0.924	0.924	0.952		1.000	0.951	0.985	0.959	0.847
<b>Molarities, millimoles/liter</b>																			
Bicarbonate (HCO3-), mmol/L	3.25	15.74	6.01	5.47	3.34	13.32	5.46	2.49	2.21	3.27	13.03	4.95	1.60		2.16	3.51	14.11	5.20	2.51
Boron, mmol/L	1.94	69.84	20.72	18.32	2.22	51.80	18.96	8.60	2.22	8.79	53.56	21.65	4.16	2.13	1.77	8.51	58.56	17.85	4.07
Calcium, mmol/L	15.77	13.32	17.59	16.59	15.47	15.97	17.04	17.17	16.99	14.25	15.69	15.69	16.17	13.67	15.14	14.40	14.92	14.52	12.82
Carbonate (CO3=), mmol/L	0.020	0.100	0.080	0.070	0.010	0.130	0.110	0.040	0.010	0.130	0.130	0.130	0.020		0.010	0.070	0.090	0.080	0.030
Chloride, mmol/L	87.17	3,159.38	885.75	803.95	93.65	2,200.28	660.08	318.76	82.93	310.30	2,273.62	685.47	150.35	66.01	81.52	310.30	2,524.68	688.29	134.27
Magnesium, mmol/L	8.93	335.66	96.67	81.04	9.46	234.47	88.03	33.32	8.72	33.36	229.54	78.57	15.92	6.87	7.45	32.33	240.23	70.75	14.15
Nitrate, mmol/L	6.43	282.21	65.80	57.09	5.84	187.07	62.73	25.00	8.64	30.48	211.26	66.92	13.74	6.77	9.11	31.77	222.54	67.25	13.71
Potassium, mmol/L	0.128	5.908	1.355	1.228	0.256	4.246	1.253	0.639	0.128	0.486	4.066	1.074	0.639	0.256	0.639	1.279	4.041	1.279	0.639
Selenium, mmol/L	0.012	0.363	0.126	0.106	0.013	0.265	0.132	0.053	0.017	0.060	0.253	0.258	0.027	0.013	0.017	0.059	0.274	0.130	0.029
Silica, mmol/L	0.523				0.488														
Sodium, mmol/L	92.61	2,775.18	985.34	885.56	102.59	1,780.48	954.16	364.83	83.57	386.65	1,808.54	891.80	166.51	81.70	77.02	361.71	1,976.93	873.09	166.82
Sulfate, mmol/L	44.34	745.29	342.46	296.66	44.55	394.50	349.74	126.99	37.37	157.18	275.84	348.70	63.39	46.01	36.85	154.05	374.73	345.58	74.42
Ca/SO4 mole ratio	0.36	0.02	0.05	0.06	0.35	0.04	0.05	0.14	0.45	0.09	0.06	0.05	0.26	0.30	0.41	0.09	0.04	0.04	0.17
<b>Ionic Strength, mmol/L</b>	276.4	7,416.3	2,439.5	2,182.7	292.9	4,898.5	2,174.7	915.0	259.8	959.2	4,901.2	2,130.9	448.7	237.1	246.8	932.4	5,446.0	2,098.5	436.3
<b>Weight Percents</b>																			
Estimated Sp Grav	1.010	1.256	1.092	1.077	1.011	1.144	1.071	1.035	1.009	1.036	1.164	1.078	1.016	1.010	1.009	1.036	1.174	1.078	1.017
Water (H2O), grams/L	998.5	963.5	986.8	989.0	998.5	979.5	989.9	995.0	998.7	994.9	976.6	988.9	997.7	998.6	998.7	994.8	975.1	988.9	997.5
Weight of liter of water, grams	1,010.5	1,255.8	1,092.1	1,077.2	1,010.5	1,143.7	1,070.6	1,034.9	1,009.2	1,035.9	1,163.6	1,077.5	1,016.2	1,009.5	1,009.1	1,036.3	1,174.5	1,077.5	1,017.4
Water (H2O), wt %	98.82%	76.72%	90.36%	91.81%	98.81%	85.64%	92.46%	96.14%	98.95%	96.04%	83.93%	91.78%	98.18%	98.92%	98.97%	96.00%	83.02%	91.78%	98.05%
Bicarbonate (HCO3-), wt %	0.0196%	0.0765%	0.0336%	0.0310%	0.0201%	0.0711%	0.0311%	0.0147%	0.0133%	0.0192%	0.0683%	0.0280%	0.0096%		0.0130%	0.0206%	0.0733%	0.0294%	0.0150%
Boron as boric acid, wt %	0.0119%	0.3439%	0.1173%	0.1051%	0.0136%	0.2801%	0.1095%	0.0514%	0.0136%	0.0525%	0.2846%	0.1242%	0.0253%	0.0130%	0.0108%	0.0508%	0.3083%	0.1025%	0.0247%
Calcium, wt %	0.0625%	0.0425%	0.0646%	0.0617%	0.0614%	0.0560%	0.0638%	0.0665%	0.0675%	0.0551%	0.0541%	0.0584%	0.0638%	0.0543%	0.0602%	0.0557%	0.0509%	0.0540%	0.0505%
Carbonate (CO3=), wt %	0.0001%	0.0005%	0.0004%	0.0004%	0.0001%	0.0007%	0.0006%	0.0002%	0.0001%	0.0008%	0.0007%	0.0007%	0.0007%		0.0001%	0.0004%	0.0005%	0.0005%	0.0002%
Chloride, wt %	0.31%	8.92%	2.88%	2.65%	0.33%	6.82%	2.19%	1.09%	0.29%	1.06%	6.93%	2.26%	0.52%	0.23%	0.29%	1.06%	7.62%	2.26%	0.47%
Magnesium, wt %	0.0215%	0.6498%	0.2152%	0.1829%	0.0228%	0.4984%	0.1999%	0.0783%	0.0210%	0.0783%	0.4795%	0.1773%	0.0381%	0.0165%	0.0179%	0.0758%	0.4972%	0.1596%	0.0338%
Nitrate, wt %	0.0395%	1.3936%	0.3736%	0.3286%	0.0358%	1.0143%	0.3633%	0.1498%	0.0531%	0.1825%	1.1258%	0.3851%	0.0838%	0.0416%	0.0560%	0.1901%	1.1750%	0.3870%	0.0835%
Potassium, wt %	0.0005%	0.0184%	0.0049%	0.0045%	0.0010%	0.0145%	0.0046%	0.0024%	0.0005%	0.0018%	0.0137%	0.0039%	0.0025%	0.0010%	0.0025%	0.0048%	0.0135%	0.0046%	0.0025%
Selenium, wt %	0.0001%	0.0023%	0.0009%	0.0008%	0.0001%	0.0018%	0.0010%	0.0004%	0.0001%	0.0005%	0.0017%	0.0019%	0.0002%	0.0001%	0.0001%	0.0004%	0.0018%	0.0010%	0.0002%
Silica, wt %	0.0031%	0.0000%	0.0000%	0.0000%	0.0029%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%
Sodium, wt %	0.29%	7.09%	2.89%	2.64%	0.33%	4.99%	2.86%	1.13%	0.27%	1.20%	4.98%	2.65%	0.53%	0.26%	0.24%	1.12%	5.40%	2.60%	0.53%
Sulfate, wt %	0.42%	5.70%	3.01%	2.65%	0.42%	3.31%	3.14%	1.18%	0.36%	1.46%	2.28%	3.11%	0.60%	0.44%</					

# Red Rock Ranch Pilot Plant Raw and Reduced Analytical Data - Page 4

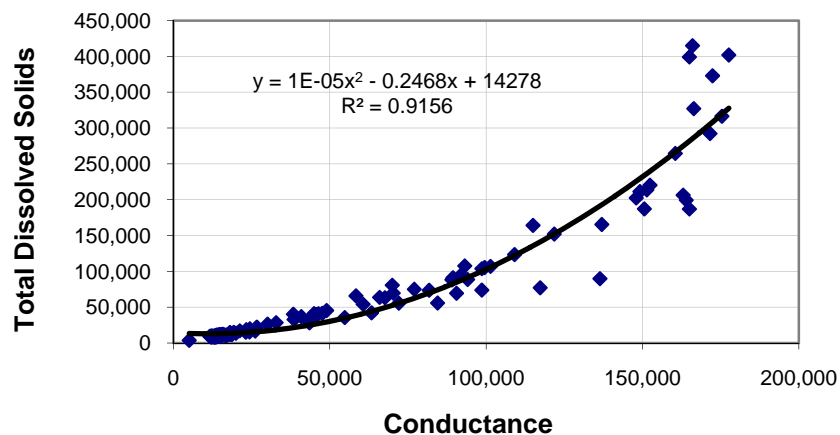
Collection Date	24-Nov-03	24-Nov-03	24-Nov-03	24-Nov-03	24-Nov-03	24-Nov-03	24-Nov-03	28-Oct-03	28-Oct-03	28-Oct-03	28-Oct-03	28-Oct-03	28-Oct-03	28-Oct-03	27-Sep-04	27-Sep-04	27-Sep-04	27-Sep-04	27-Sep-04	27-Sep-04	17-Sep-04	Average	Std Dev
Station	Sump D	TT1	TT2	TT3	TT4	Slt Crystal TT-3	S.E.D	Sump D	TT1	TT2	TT3	TT4	S.E.D	RRR-S.B.	Sump C	Sump D	TT3	TT4	TT3 salt	S.E.D			
Conductance (EC) uS/cm	13,970	32,860	49,010	150,600	93,180	5,070	21,260	12,110	40,910	70,320	148,000	92,030	30,130	160,500	15,800		165,000	137,000	81,800	60,700			
Dissolved Bicarbonate (HCO3-) (as CaCO3)	277	252	371	1306	625	6	289	266	316	492	1090	622	252			252	2687	935	111	395			
Dissolved Boron (mg/L)	21	70.4	109	607	230	1.3	37.4								25.4	18.6	1480	390	36.4	130			
Dissolved Calcium (mg/L)	601	592	602	678	577	10	586	562	633	565	469	647	598		583	561	200	603	178	586			
Dissolved Carbonate (CO3=) (as CaCO3)	2	4	10	10	13	1	5	1	5	16	11	16	4			1	5	12	4	6			
Dissolved Chloride (mg/L)	2,700	7,270	11,400	80,000	29,300	142	4,400	1,650	8,080	17,900	69,000	29,300	5,700	87,200	2,390	2,220	156,200	50,100	25,100	14,000			
Dissolved Magnesium (mg/L)	197	543	858	5,990	2,250	12	315	165	706	1,380	4,570	2,300	485	5,600	194	160	3,450	3,530	373	930			
Dissolved Nitrate (mg/L)	480	1,280	2,040	13,700	5,590	31	774	319	1,560	3,370	11,500	5,030	1,100		474	318	28,300	8,360	753	2,320			
Dissolved Potassium (mg/L)	10	14.8	22.3	173	55	5	25	5	25	50	125	57	25		10	2.4	90	112	50	32			
Dissolved Selenium (mg/L)	1.25	3.29	4.98	19.6	10.4	0.477	1.35	0.823	4.06	8.65	24	13.2	2.92	33.2	1.06	0.803	39.2	15.8	4.66	5.3			
Dissolved Silica (SiO2) mg/L	33.2							35								30.6							
Dissolved Sodium (mg/L)	2,820	8,710	14,200	59,000	30,700	1,250	4,880	2,330	10,200	22,100	59,500	33,200	8,190	78,600	3,340	2,580	137,000	54,300	26,500	16,700			
Dissolved Sulfate (mg/L)	4,160	10,800	18,000	32,100	39,300	2,490	6,510	4,640	15,300	28,200	30,200	35,100	12,000	84,400	4,590	3,300	84,600	50,600	23,800	18,100			
Dissolved Hardness (as CaCO3)	2,313	3,715	5,037	26,364	10,708	53	2,761	2,083	4,489	7,095	19,993	11,089	3,491		2,255	2,060	14,420	16,045	1,819	5,294			
pH	7.8	8.2	8.4	7.9	8.3	6.2	8.2	7.7	8.2	8.5	8	8.4	8.2		7.5	7.6	7.3	8.1		8.2			
Total Alkalinity (mg/L) (as CaCO3)	279	256	380	1,316	637	6	293	267	321	507	1,100	637	256		271	253	2,692	946		401			
Total Dissolved Solids (mg/L)	10,780	28,440	45,360	187,200	107,600	3,682	17,030	9,792	36,900	69,600	202,400	95,100	26,420	264,600	12,070	9,380	399,200	165,500	73,600	53,960			
Sum of dissolved solids (mg/L)	11,302	29,539	47,617	193,584	108,650	3,949	17,823	9,974	36,829	74,082	176,489	106,285	28,357		11,607	9,444	414,051	168,958	76,910	53,204			
Concentration ratios																							
Boron Conc Ratio	1.000	3.352	5.190	28.905	10.952	0.062	1.781									1.000	79.570	20.968	1.957	6.989			
Chloride Conc Ratio	1.000	2.693	4.222	29.630	10.852	0.053	1.630	1.000	4.897	10.848	41.818	17.758	3.455			1.000	70.360	22.568	11.306	6.306			
Magnesium Conc Ratio	1.000	2.756	4.355	30.406	11.421	0.061	1.599	1.000	4.279	8.364	27.697	13.939	2.939			1.000	21.563	22.063	2.331	5.813			
Nitrate Conc Ratio	1.000	2.667	4.250	28.542	11.646	0.065	1.613	1.000	4.890	10.564	36.050	15.768	3.448			1.000	88.994	26.289	2.368	7.296			
Potassium Conc Ratio	1.000	1.480	2.230	17.300	5.500	0.500	2.500	1.000	5.000	10.000	25.000	11.400	5.000			1.000	37.500	46.667	20.833	13.333			
Selenium Conc Ratio	1.000	2.632	3.984	15.680	8.320	0.382	1.080	1.000	4.933	10.510	29.162	16.039	3.548			1.000	48.817	19.676	5.803	6.600			
Sodium Conc Ratio	1.000	3.089	5.035	20.922	10.887	0.443	1.730	1.000	4.378	9.485	25.536	14.249	3.515			1.000	53.101	21.047	10.271	6.473			
Sulfate Conc Ratio	1.000	2.596	4.327	7.716	9.447	0.599	1.565	1.000	3.297	6.078	6.509	7.565	2.586			1.000	25.636	15.333	7.212	5.485			
Sulfate Conc Ratio, Ca & HCO3 corrected	1.000	3.331	5.867	10.904	13.398	0.866	1.839	1.000	4.074	7.917	8.653	9.895	3.124			1.000	41.137	23.891	11.283	8.132			
Bicarbonate Conc Ratio	1.000	0.910	1.339	4.715	2.256	0.022	1.043	1.000	1.188	1.850	4.098	2.338	0.947			1.000	10.663	3.710	0.440	1.567			
Calcium Conc Ratio	1.000	0.985	1.002	1.128	0.960	0.017	0.975	1.000	1.126	1.005	0.835	1.151	1.064			1.000	0.357	1.075	0.317	1.045			
Molarities, millimoles/liter																							
Bicarbonate (HCO3-), mmol/L	2.77	2.52	3.71	13.05	6.24	0.06	2.89	2.66	3.16	4.92	10.89	6.21	2.52			2.52	26.85	9.34	1.11	3.95			
Boron, mmol/L	1.94	6.51	10.08	56.15	21.28	0.12	3.46								2.35	1.72	136.91	36.08	3.37	12.03			
Calcium, mmol/L	15.00	14.77	15.02	16.92	14.40	0.25	14.62	14.02	15.79	14.10	11.70	16.14	14.92		14.55	14.00	4.99	15.04	4.44	14.62	14.20	4.04	
Carbonate (CO3=), mmol/L	0.020	0.040	0.100	0.100	0.130	0.010	0.050	0.010	0.050	0.160	0.110	0.160	0.040			0.010	0.050	0.120	0.040	0.060			
Chloride, mmol/L	76.16	205.08	321.58	2256.70	826.52	4.01	124.12	46.54	227.93	504.94	1946.40	826.52	160.79	2459.80	67.42	62.62	4406.21	1413.26	708.04	394.92			
Magnesium, mmol/L	8.10	22.34	35.29	246.40	92.55	0.49	12.96	6.79	29.04	56.77	187.99	94.61	19.95	230.36	7.98	6.58	141.92	145.21	15.34	38.26			
Nitrate, mmol/L	7.74	20.64	32.90	220.93	90.15	0.50	12.48	5.14	25.16	54.35	185.45	81.12	17.74		7.64	5.13	456.38	134.82	12.14	37.41			
Potassium, mmol/L	0.256	0.379	0.570	4.425	1.407	0.128	0.639	0.128	0.639	1.279	3.197	1.458	0.639		0.256	0.061	2.302	2.864	1.279	0.818			
Selenium, mmol/L	0.016	0.042	0.063	0.248	0.132	0.006	0.017	0.010	0.051	0.110	0.304	0.167	0.037	0.420	0.013	0.010	0.496	0.200	0.059	0.067			
Silica, mmol/L	0.553							0.582								0.509							
Sodium, mmol/L	87.93	271.59	442.78	1839.73	957.28	38.98	152.17	72.65	318.05	689.12	1855.32	1035.24	255.38	2450.89	104.15	80.45	4271.91	1693.17	826.32	520.74			
Sulfate, mmol/L	43.30	112.42	187.36	334.13	409.08	25.92	67.76	48.30	159.26	293.54	314.35	365.36	124.91	878.53	47.78	34.35	880.61	526.70	247.74	188.40			
Ca/SO4 mole ratio	0.35	0.13	0.08	0.05	0.04	0.01	0.22	0.29	0.10	0.05	0.04	0.04	0.12		0.30	0.41	0.01	0.03	0.02	0.08			
Ionic Strength, mmol/L	258.2	671.1	1064.5	5005.7	2433.6	70.7	405.8	210.3	794.9	1633.2	4527.3	2443.0	611.8		266.7	221.4	10333.6	3991.8	1824.3	1225.9			
Weight Percents																							
Estimated Sp Grav	1.009	1.025	1.040	1.164	1.094	1.003	1.015	1.009	1.032	1.061	1.177	1.083	1.023	1.232	1.011	1.008	1.349	1.145	1.064	1.047			
Water (H2O), grams/L	998.7	996.4	994.3	976.6	986.6	999.5	997.9	998.8	995.4	991.3	974.7	988.1	996.7	966.9		998.8	950.1	979.3	990.8	993.3			
Weight of liter of water, grams	1009.4	1024.9	1039.7	1163.8	1094.2	1003.2	1014.9	1008.6	1032.3	1060.9	1177.1	1083.2	1023.1	1231.5	1010.6	1008.2	1349.3	1144.8	1064.4	1047.2			
Water (H2O), wt %	98.93%	97.23%	95.64%	83.91%	90.17%	99.63%	98.32%	99.03%	96.43%	93.44%	82.81%	91.22%	97.42%	78.51%	98.81%	99.07%	70.41%	85.54%	93.09%	94.85%			
Bicarbonate (HCO3-), wt %	0.0167%	0.0150%	0.0218%	0.0684%	0.0348%	0.0004%	0.0174%	0.0161%	0.0187%	0.0283%	0.0565%	0.0350%	0.0150%			0.0152%	0.1214%	0.0498%	0.0064%	0.0230%			
Boron as boric acid, wt %	0.0119%	0.0393%	0.0600%	0.2983%	0.1202%	0.0007%	0.0211%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0000%	0.0144%	0.0106%	0.6274%	0.1949%	0.0196%	0.0710%			
Calcium, wt %	0.0595%	0.0578%	0.0579%	0																			



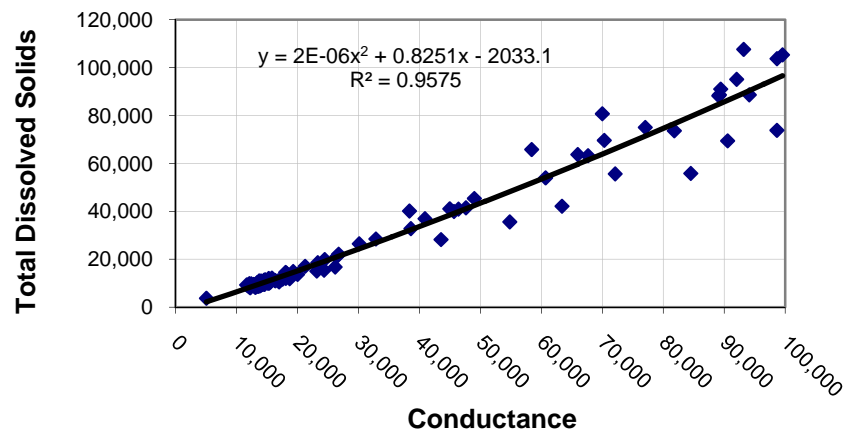
## Concentration Ratios vs. Chloride Concentration Ratio



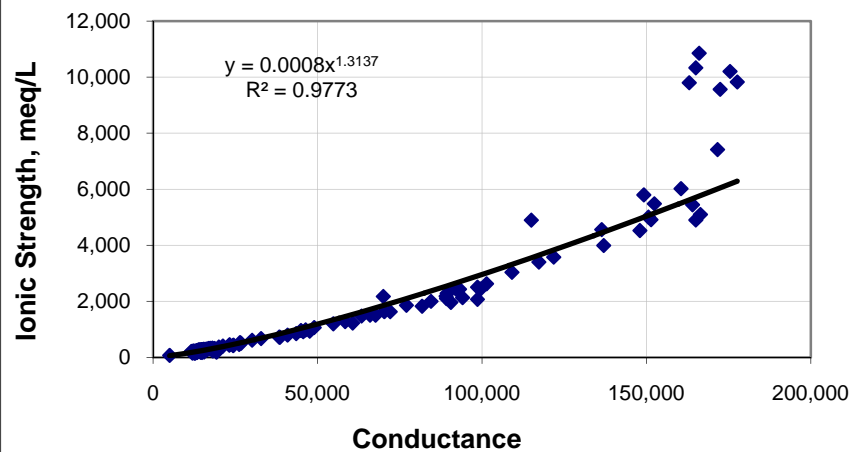
**Total Dissolved Solids vs. Conductance  
All Data**



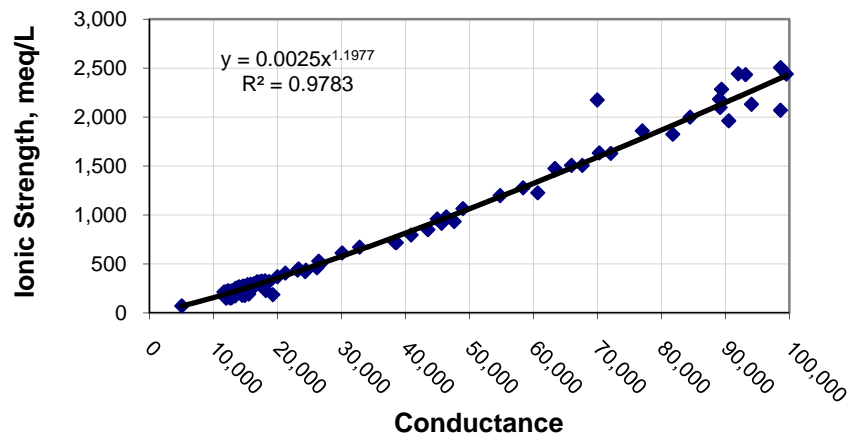
**Total Dissolved Solids vs. Conductance  
Excludes Conductance Data Over 100,000  $\mu$ S/cm**



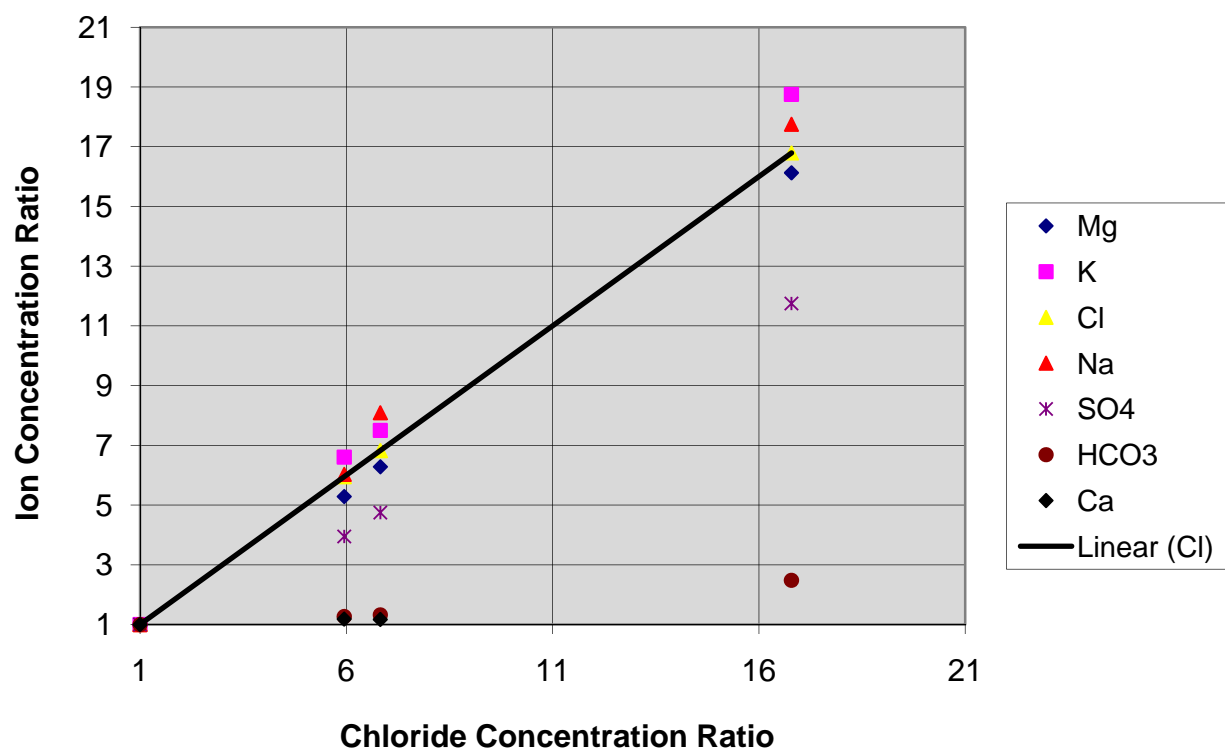
**Ionic Strength vs. Conductance  
All Data**



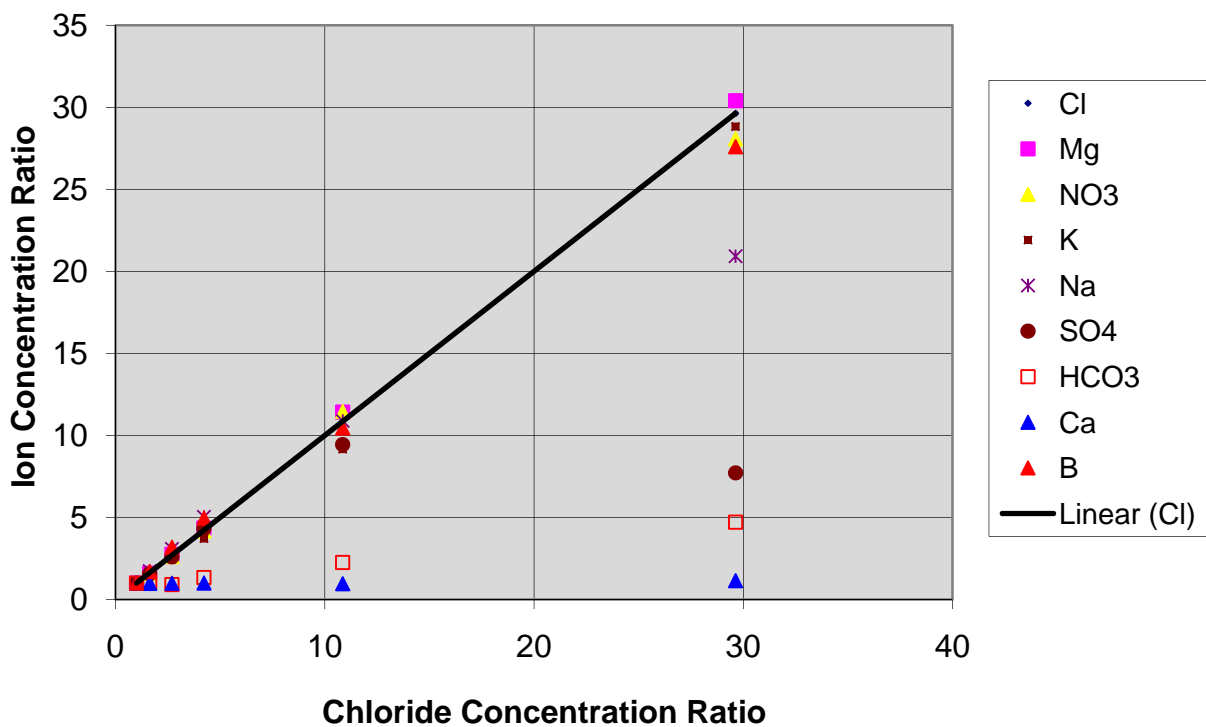
**Ionic Strength vs. Conductance  
Excludes Conductance Data Over 100,000  $\mu$ S/cm**



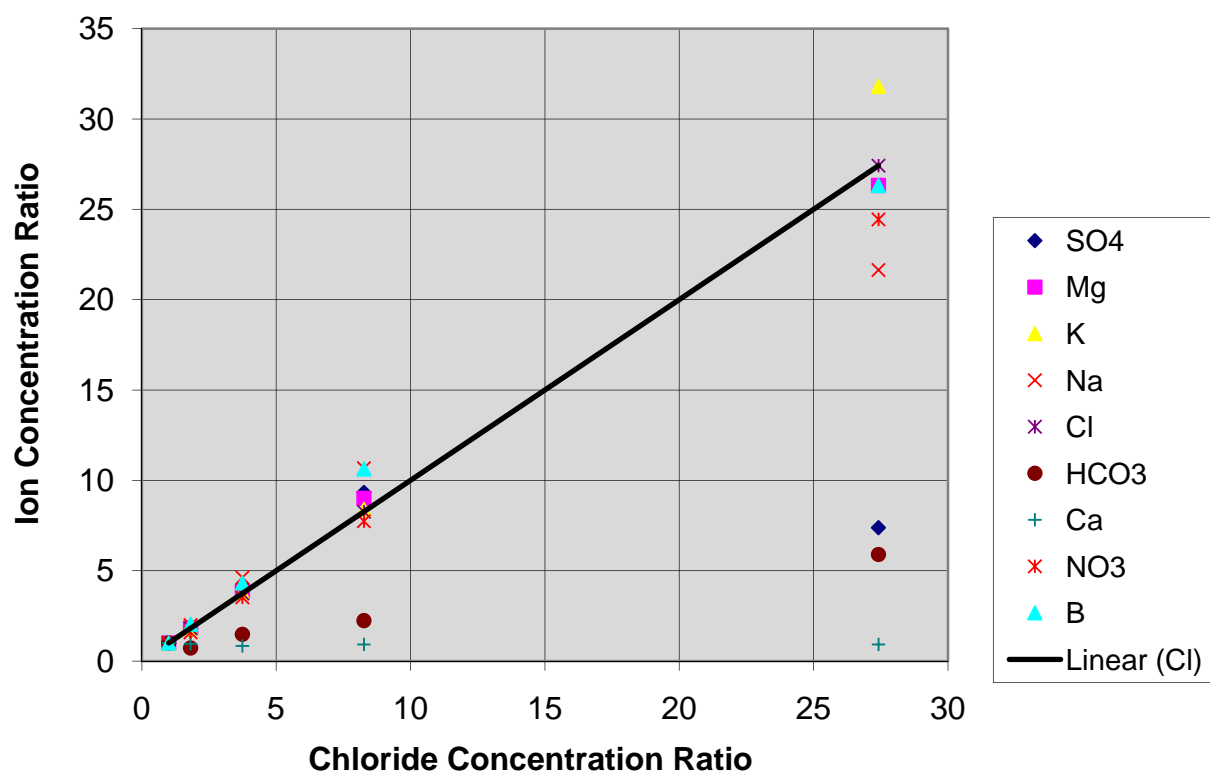
# Concentration Ratios vs. Chloride C.R. 29 July 2003



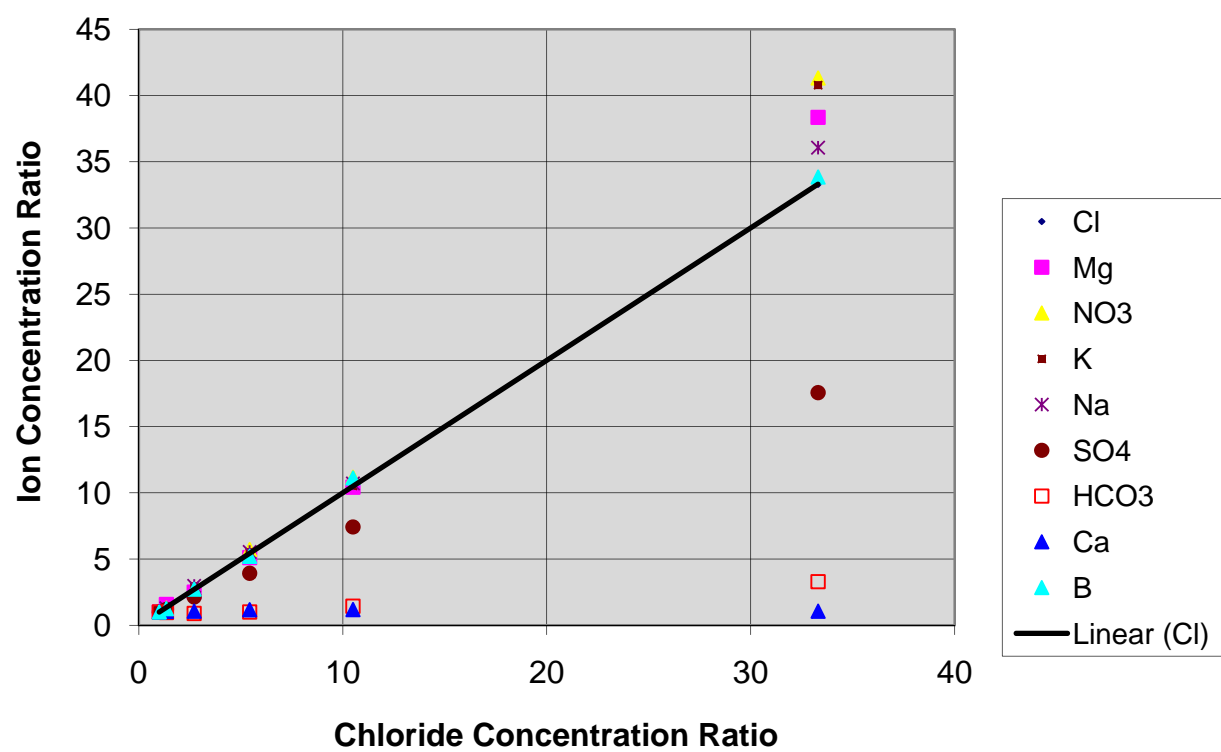
**Concentration Ratio vs. Chloride C.R.**  
**29 Nov 2003**



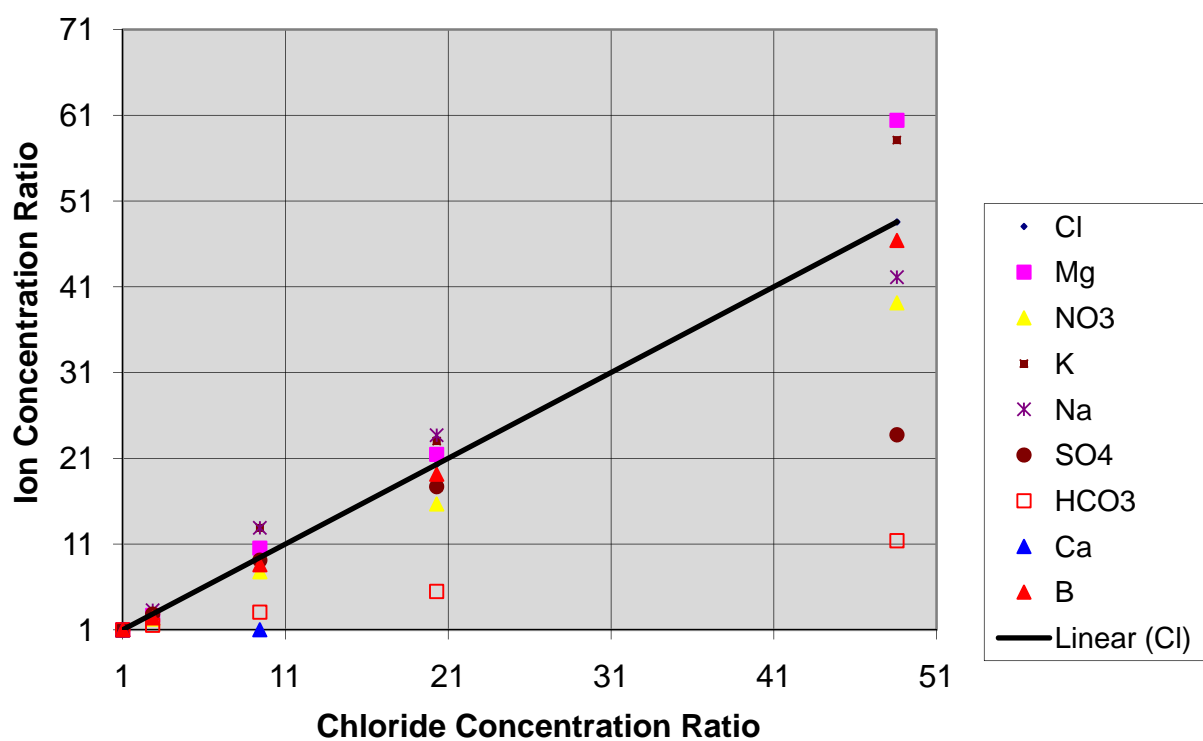
**Concentration Ratio vs. Chloride C.R.**  
**28 Jan 2004**



# Concentration Ratio vs. Chloride C.R. 29 Mar 2004



# **Concentration Ratio vs. Chloride C.R.** **31 Aug 2004**



## Expected Solar Radiation at Red Rock Ranch

Time of year	Maximum Expected Solar Radiation*, BTU/(hr)(ft <sup>2</sup> )	Cloud factor, fraction obscured	Assumed Wet Surface Emissivity	Expected Solar Radiation at Red Rock Ranch, BTU/(hr)(ft <sup>2</sup> )
1-Jan	49.0	0.58	0.95	19.6
15-Jan	56.5	0.55	0.95	24.2
1-Feb	64.0	0.52	0.95	29.2
15-Feb	74.0	0.50	0.95	35.2
1-Mar	84.0	0.40	0.95	47.9
15-Mar	94.0	0.30	0.95	62.5
1-Apr	104.0	0.20	0.95	79.0
15-Apr	112.0	0.15	0.95	90.4
1-May	120.0	0.10	0.95	102.6
15-May	125.0	0.10	0.95	106.9
1-Jun	130.0	0.10	0.95	111.2
15-Jun	132.0	0.10	0.95	112.9
1-Jul	130.0	0.10	0.95	111.2
15-Jul	127.5	0.10	0.95	109.0
1-Aug	125.0	0.10	0.95	106.9
15-Aug	117.3	0.10	0.95	100.2
1-Sep	109.5	0.10	0.95	93.6
15-Sep	99.0	0.15	0.95	79.9
1-Oct	89.0	0.20	0.95	67.6
15-Oct	79.0	0.30	0.95	52.5
1-Nov	69.0	0.40	0.95	39.3
15-Nov	61.5	0.50	0.95	29.2
1-Dec	54.0	0.53	0.95	24.1
15-Dec	46.0	0.55	0.95	19.7

\* Data from Perry's Chemical Engineers' Handbook, 7th ed.



## **APPENDIX B – Published Information**

### **Table of Contents**

- B-1 “Perry’s Chemical Engineers’ Handbook,” 7<sup>th</sup> Edition, p. 12-21 through 12-25
- B-2 “Handbook of Chemical Engineering Calculations,” 2<sup>nd</sup> Edition, by Nicholas P. Chokey, sect. 16-14
- B-3 “Evaluation of Solar Pond Performance for the Years 1968, 1969 and 1970,” Internal Memo, Kerr-McGee Chemical Corp., by J. L. Fairchild
- B-4 San Joaquin Valley Unified Air Pollution Control District, Rule 4202
- B-5 “The Oxidation States of the Elements and Their Potential in Aqueous Solution,” 2<sup>nd</sup> Edition, by Wendell M. Latimer, Prentice-Hall, Inc, 1952, pp. 135, 319, 320, 321, 322, 323
- B-6 “Solubilities, Inorganic and Metal-Organic Compounds, Volume II,” 4<sup>th</sup> Edition, by William F. Linke, Ph. D, American Chemical Society, 1965
- B -7 “Sodium Sulfate,” United States Geological Survey publication for 2004, by Dennis Kostick
- B-8 “Potash: Deposits, Processing, Properties and Uses,” by Donald E. Garrett, PhD, Chapman & Hall Co., 1996
- B-9 “Chlorine: World Outlook,” by Ron Van Santen, June 1998